THE LEAD DIOXIDE ELECTRODE

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I. Introduction

Current technological developments, for instance in electrochemical power sources, are creating fresh interest in the fundamental properties of solid oxide electrodes. Of these, lead dioxide has attracted considerable attention owing to its use as the active material in the positive plate of the lead–acid cell, and there exists a considerable amount of literature concerning the behavior of this electrode. Several past reviews[1-5] have devoted limited sections to the consideration of the lead dioxide electrode. However, since papers describing phenomena have been largely technological and experimental techniques have not always provided kinetic data adequate to test theories of mechanism, experimental papers are discussed, in which it seems to the present authors that the measurements have been significant in understanding the processes at the lead dioxide electrodes.

For measurements on any solid electrodes the experimental requirements are severe. In the present case lead dioxide should be carefully prepared and manipulated, both mechanically and electrochemically; a rigorous standard of electrolyte cleanliness is necessary and consequently special techniques of measurement are required. The interpretations of the resulting measurements have often left a good deal of speculation and suggested many more experiments rather than providing final conclusions.

Adequate techniques and satisfactory experimental standards have sometimes resulted from the recognition of the inadequacies of early experiments. A very selective review may do less than justice to much good work; however, it seems that a more rational approach is required than to accumulate measurements from poorly controlled experiments.

In general, oxides are nonconducting or semiconducting; however, there exist a limited number which show electrical conductivity and bear close similarities to metals. Lead dioxide is such an oxide, and consequently an electrical double layer forms in the interphase between the lead dioxide electrode and an electrolyte solution in much the same way as at a metal electrode. Since exchange proceeds through this electrical double layer, it is desirable that its properties should be known and understood. In general, quantitative interpretation of double layer measurements at solid oxide electrodes, comparable with the established knowledge of the ideal polarizable electrode, as exemplified by Hg, is not available. Capacitance measurements seem most promising, but experimental difficulties are considerable. Many oxides carry adsorbed films which, once formed, are relatively permanent even where a range of quasi-ideal polarizability exists. These cause "hysteresis" effects in capacitance measure-

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ments made after an electrode has been subjected to quite small potential excursions. Such adsorption also results in a frequency dependence of the electrode impedance. However, some frequency dependence in electrode impedances is found even with metals of high hydrogen overvoltage with macroscopically smooth surfaces in exhaustively cleaned solutions of indifferent electrolytes. At present it is suggested that this small residual frequency dependence is a spurious effect; de Levie[6] has reviewed these effects.

The difficulties encountered with solid metal electrodes will also be expected to apply in the case of solid oxide electrodes. In addition, there are several further factors to be considered related to the structure of oxides.[6a] These include the participation in electrode reactions of both oxygen and metal atoms which differ from each other in size. The electronegativity of each atom is also generally different which infers that the bonding electrons are not equally shared between the metal and oxygen atoms. Metals can exist in more than one oxidation state because of the presence of partially filled orbitals, and hence various stoichiometries have also to be considered.

II. Preparation of Lead Dioxide

In most of the earlier reported preparations of lead dioxide no attention was paid to the polymorphic form of the product. However, in some more recent papers details of preparations are given in which careful control of the product morphology has been achieved. The various methods[7-30] for the preparation of lead dioxide that have been proposed from time to time may be subdivided into chemical preparations and electrolytic preparations.

Lead dioxide has been prepared chemically by methods in which Pb(II) compounds are oxidized to lead dioxide in the solution phase or in melts or by heating at elevated temperatures in oxygen. It was reported that lead dioxide could be prepared by the thermal oxidation of PbO[7] or Pb_3O_4;[8] however, White and Roy[9] examined the products by X-ray diffraction and found that the oxide produced corresponded to an oxide with an active oxygen content of $PbO_{1.582}$; *i.e.*, it was not possible to produce an oxide by this method with oxygen in excess of $Pb_{12}O_{19}$. Lead dioxide may also be prepared by the hydrolysis of lead(IV) salts;[31] for example, lead tetrachloride may be hydrolyzed in cold hydrochloric acid solution,[10] or a saturated solution of lead tetraacetate may be hydrolyzed in glacial acetic acid. The majority of preparations, however, involve the oxidation of lead(II) salts. Chemical oxidations of sodium plumbite solution in alkali are readily achieved with chlorine, bromine, and hydrogen peroxide[10] and simple lead(II) salts may be oxidized with 37 *M* nitric acid.[10] Anodic oxidations may be carried out with alkaline solutions of sodium plumbite or acid solutions of nitrates, perchlorates, fluoroborates, or fluorosilicates. The anodic oxidation of lead sulfate is well known.[11]

A. PURE LEAD DIOXIDE

The use of lead dioxide in electrolytic systems, particularly for thermodynamic measurements, has indicated that irreproducible results are often obtained, and this imposes stringent purity requirements on the materials involved. For example, in the work of Hamer,[12] who studied the galvanic cell

$$H_2\ (1\ atm),\ Pt|H_2SO_4(m),\ PbSO_4,|lead\ dioxide,\ Pt$$

methods for preparing lead dioxide in a suitably stable form were investigated since commerical samples gave erratic emf results no matter how they were treated before use. The products of the oxidation of alkaline plumbite solutions by chlorine, bromine, or hydrogen peroxide were similarly unsatisfactory. Hamer[12] suggested that the electrolysis of an aqueous solution containing lead nitrate and concentrated nitric acid, maintained at 93° with use of a platinum gauze anode, produced the most consistent potential values. A platinum wire cathode, surrounded by a porous cup, was used and the solution continuously stirred. In agreement with previous observations[13] it was found to be essential to digest the black powder so formed at 100° with 3 *M* sulfuric acid for 7 days. This apparently converted the dioxide to its most stable form and removed any lower oxide by conversion to sulfate. Chemical analysis, of which the work of Bagshaw, *et al.*,[14] is typical of many investigations, has shown that lead dioxide, as prepared by any method so far investigated, always contains a deficiency of oxygen from that required for stoichiometry.

B. CONFORMATION OF LEAD DIOXIDE TO PbO_2

A considerable amount of effort has been made into forcing lead dioxide to conform to exact stoichiometry. The methods used include chemical oxidation, direct oxidation at high

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(6a) The requirements of an "ideal" oxide electrode can be summarized as (1) perfect lattice containing no holes, fissures, grain boundaries, impermeable to the electrolyte; (2) readily obtainable in a reproducible state of minimum free energy; (3) nonreactive nature, so that it is stable in the electrolyte and free from films; (4) no adsorption of reactant ions at the interphase or the presence of adsorbed intermediates and/or reaction products on the surface which will cause the concentration of soluble electroactive ions in the bulk to differ from that at the interphase; (5) small size difference between the metal atom and oxygen atom in the lattice.
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(31) A. Seidell and W. F. Linke, "Solubilities of Inorganic Compounds," 4th ed, Wiley, New York, N. Y., 1958.

temperatures using high oxygen pressures, and the crystal growth of stoichiometric lead dioxide in the solution phase. The starting material for these experiments has in the main been lead dioxide of "normal composition."

The most exhaustive attempts to form stoichiometric lead dioxide by direct union of elements appear to have been by Duisman and Giaque.[10] These include oxidation of lead dioxide at elevated temperatures and high oxygen pressures; for example, a slurry of chemically prepared lead dioxide in 5 *M* sodium hydroxide was treated with oxygen at pressures up to ~8000 psig (1 psig ≡ 6.895 kN/m²) and temperatures up to 320° for as long as 2 weeks. It was reported[10] that at the extreme conditions small crystals were formed, but analysis showed the oxygen content to be only ~98% of the theoretical for lead dioxide. In every case, it was found that the product had a deficiency of active oxygen. The addition of solid oxidants and oxidizing melts to lead dioxide dispersions, followed by reaction at high temperatures and oxygen pressures as high as ~4000 psig, also failed to yield stoichiometric lead dioxide.[10]

Duisman and Giaque[10] also attempted to convert powdered lead dioxide into the crystalline form by dissolving lead dioxide in a suitable solvent and slowly recrystallizing out lead dioxide under a pressure of 1 atm. The starting material for all of these experiments was commerical lead dioxide and the solvent concentrated nitric acid, in 1 : 2, 1 : 1, and 2 : 1 dilutions with water. The lead dioxide–nitric acid mixture was mechanically agitated for periods up to 6 months at 35°. The lead dioxide was inspected under a microscope before and after this treatment, and no evidence of increased particle size was observed, but analysis indicated that the active oxygen content of the material had decreased. Experiments at 100° for shorter periods of time showed a similar decrease in active oxygen. Other solvents were investigated: perchloric acid ($HClO_4 \cdot 2H_2O$), hydrofluoric acid (48%), sodium hydroxide (various concentrations), formic acid, acetic acid (various concentrations), and acetic acid with 10% acetic anhydride; all were found to be unsuccessful. Liquid ammonia was also tested as a solvent since lead dioxide has properties in common with metals, but it was found that PbO_2 did not result from this treatment.

C. ELECTROLYTIC PREPARATIONS

Of various inert materials available as anodes for the electrodeposition of lead dioxide, Pt and Au are the most suitable. Various electrolytes have been employed. A nearly saturated solution of lead perchlorate in perchloric acid–water eutectic[15] was electrolyzed at anode current densities of 1 and 2 mA/cm², using a platinum anode and a graphite cathode at temperatures near −50°. Analysis of the product gave 96.4% of the theoretical active oxygen for lead dioxide, with no significant difference between materials prepared at the different current densities. Also employed have been solutions of lead perchlorate in water, lead acetate in water and in glacial acetic acid, lead nitrate in various nitric acid concentrations, and solutions of sodium plumbite at various concentrations of plumbite and sodium hydroxide.

The effect of hydrogen ion concentration on the lead dioxide electrodeposit was investigated by Duisman and Giaque[10] using lead nitrate–nitric acid solutions in water. Neutral lead nitrate solution was added to the electrolysis solution at such a rate to maintain the concentration of nitric acid at a fixed value. Experiments were made in the range from nearly neutral solutions to a hydrogen ion concentration of 2 *M*. At the highest acidities, the active oxygen content of the product declined; however, there was no clear evidence that a solution of 0.1 *M* HNO_3 engendered a different product than one with 1.0 *M* HNO_3. It was suspected that NO_2^- ions, formed at the cathode by reduction, may have an adverse effect on the oxygen content of the sample. This possibility was investigated and eliminated through the use of a solution of lead nitrate and copper nitrate as electrolyte, since Collat and Lingane[32] have shown that electrolytic reduction of nitrate ions proceeds all the way to NH_4^+ in the presence of Cu^{2+}. No change in the active oxygen content of the samples produced was observed. However, there is no doubt of the complication caused by the NO_3^-–NO_2^- process which results in a very serious decline in deposition efficiency if the NO_3^-/NO_2^- concentration ratio falls below 0.99. In the case of the lead nitrate solutions, Duisman and Giaque[10] also examined the effect of rotating the anode at different speeds. It was observed that at high speeds the porosity of the sample was slightly decreased. The products, prepared at speeds higher than 100 rpm, all had essentially the same active oxygen content. Current density has no significant effect on the active oxygen content of the lead dioxide deposit. However, the samples prepared at low current densities had a more crystalline appearance and are generally of much better mechanical strength.

From the efforts of a number of workers,[10,32-35] a formula in the region of $PbO_{1.98}$ appears to best represent lead dioxide although it should be emphasized that the analysis of lead dioxide specimens by X-ray techniques is complicated[14] particularly by the suggested formation of a new phase at $PbO_{1.9}$.[33,36] For example, Butler and Copp[36] found the first traces of a second phase, α-PbO_x, in a decomposition product, $PbO_{1.935}$. Arbitrarily assuming that α-PbO_x, would not become visible until it represented at least 5% of the sample, and that its composition was Pb_7O_{11}, they then calculated that the lower limit of composition for lead dioxide was $PbO_{1.95}$. A further complication was that Pb_5O_8 and lead dioxide have essentially the same diagonal lattice.[37,38]

The existence of the two polymorphs, α- and β-lead dioxide, has been studied in great detail.[14] The following methods have been used successfully for the production of the two polymorphs.

1. α-Lead Dioxide

a. Oxidation of Yellow Lead Monoxide by a Fused Sodium Chlorate–Sodium Nitrate Mixture

Yellow lead monoxide (50 g), sodium chlorate (20 g), and sodium nitrate (40 g) were mixed and heated in a nickel crucible to 340° for 10 min. The resulting black melt was treated with water to remove soluble salts. After drying, the dark brown powder was mixed with the same quantities of sodium chlorate and sodium nitrate and the fusion repeated. This

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product was washed with water to remove any soluble material and then suspended in 500 ml of 3 *M* nitric acid solution to remove the divalent lead ions from the lattice. After being kept overnight, the suspension was heated to 60°, filtered, and washed with water. It was important that the temperature did not rise above 340° for any length of time as this reduced the material to minium, Pb_3O_4, which would form the α modification on dissolution of the divalent lead ions. It was also important that the divalent lead in the fusion product was removed by nitric acid and not by ammonium–acetic acid solution, as the latter also produced mixtures of α- and β-lead dioxide.[39,40]

b. Oxidation of Sodium Plumbite by Chlorine Dioxide

Yellow lead monoxide (50 g) was added to 500 ml of water containing 20 g of sodium hydroxide. The mixture was stirred and chlorine dioxide blown in by a stream of air for 4 hr. The resulting sodium chlorite–lead dioxide mixture was filtered, washed with water, and finally boiled with 3 *M* nitric acid for 45 min to remove any lead monoxide. The product was then washed with water and dried.

c. Oxidation of Lead Acetate by Ammonium Persulfate[39,40]

Ammonium persulfate (250 g) was added to 250 ml of water and 1 l. of saturated ammonium acetate solution. An aqueous saturated lead acetate solution, containing 325 g of lead acetate, was then added slowly, simultaneously with 300 ml of 58% NH_4OH. The reaction proceeded slowly. After 6 hr an additional quantity of 50 g of ammonium persulfate was added and the solution stirred for 24 hr. It was then heated to 70° for a short period of time to drive off excess NH_3 and to dissolve any precipitated divalent lead compounds. The precipitate was filtered and washed with ammonium acetate solution and water and finally dried at room temperature.

d. Other Methods

Other methods include alkaline formation of lead battery positive plates (Voss and Freundlich[41]) and electrooxidation of lead acetate in an alkaline solution (Zaslavskii[44,45]).

2. β-Lead Dioxide

β-Lead dioxide can be prepared by (i) acid formation of lead battery positive plates[24] or (ii) electrooxidation of lead perchlorate.[14] In the latter method lead monoxide (195 g) was added to 500 ml of 2 *M* perchloric acid solution. A platinum anode and a lead cathode were suspended in the solution and a current of density 2.5 mA cm^{-2} was passed. The deposit was removed, ground, and washed with water.

Another preparation (iii) is electrooxidation of lead acetate in acid solution.[14] Lead acetate (100 g) was dissolved in 0.5 *M* acetic acid solution. A platinum anode and lead cathode were suspended in the solution and a current of density 1.0 mA cm^{-2} was passed. The deposit was ground and washed with water.

III. Physical Characteristics and Properties

A. CRYSTAL STRUCTURE

Following the work of Kameyama and Fukumoto,[42] Tolkachev,[43] Zaslavskii and coworkers,[44,45] Golovanov,[46] Thomas,[47] Darbyshire[8] and Huggins,[48] the structures of α- and β-lead dioxide are now generally agreed.

α-Lead dioxide has the orthorhombic structure of columbite[25,26] and has the space group *Pbcn* (V_h^{14}). β-Lead dioxide has the tetragonal rutile structure[8,46–48] which belongs to the space group *P4/mnm* (D_{4h}^{14}). It was shown first by Pauling and Sturdivant[49] that a close relationship exists between the two lattices. In both cases, each metal ion is in the center of a distorted octahedron. The essential difference is in the way in which the octahedra are packed, as is illustrated in Figure 1. In β-PbO_2, neighboring octahedra share opposite edges, which results in the formation of linear chains of octahedra. Each chain is connected with the next one by sharing corners. In α-PbO_2, neighboring octahedra share nonopposing edges in such a way that zig-zag chains are formed. Each chain is connected with the next one by sharing corners. The general relationship for the polymorphism of pairs of similar oxides has been discussed elsewhere.[50–53]

Only in the case of β-lead dioxide have the oxygen positions actually been determined;[54] however, the Pb–O distances are thought to be the same in both modifications.[55] α- and β-lead dioxide may be distinguished from each other by means of X-ray analysis. This method has been used extensively to estimate the proportion of polymorphs in a mixture of the two by means of the standard diffraction patterns.

B. STANDARD DIFFRACTION PATTERNS[56] FOR α- AND β-LEAD DIOXIDES

Standard diffraction patterns for the lead dioxides are listed in Table I.

The technique of X-ray analysis is straightforward in principle,[20,57] but in the case of lead dioxide it presents certain problems. These arise because of small crystallite size, lattice distortion, preferred orientation, superposition of diffrac-

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(55) J. Leciejewicz and I. Padlo, *Naturwissenschaften*, **49**, 373 (1962).
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Table I

Standard Diffraction Pattern for α- and β-Lead Dioxides

Interplanar spacing	*Rel intensity*	*Indices hkl*
	α-Lead Dioxide	
3.83	12	110
3.12	100	111
2.97	15	020
2.74	70	002
2.63	70	021
2.48	20	200
2.23	6	112
2.02	6	022
1.89	30	220
1.84	45	130, 202
1.79	30	221
1.64	15	113
1.56	17	222, 023
1.53	30	311, 132
1.43	20	041, 312
1.37	15	312
1.31	15	233
1.26	20	330
1.24	30	241, 400
1.20	40	204, 313
	β-Lead Dioxide	
3.50	100	110
2.80	100	101
2.48	70	200
2.21	10	210
1.856	100	211
1.754	60	220
1.693	40	002
1.569	60	310
1.527	70	112
1.486	70	301
1.399	50	202
1.276	70	321
1.240	20	400
1.220	50	222
1.170	20	330
1.152	70	312

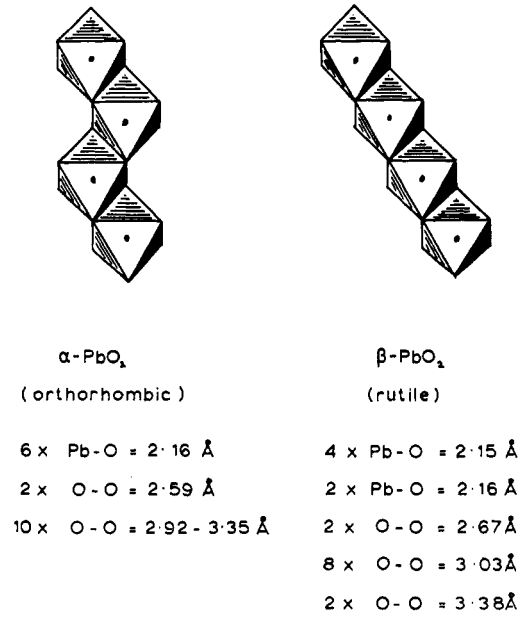

Figure 1. Packing of oxygen octahedra in α- and β-lead dioxide from ref 29 by permission of the *Journal of the Electrochemical Society*. Lead–oxygen and oxygen–oxygen distances as determined in ref 45 and 55.

tion peaks, and internal absorption effects as described by a number of workers.[14,58-62] In standard mixtures of the two polymorphs, which contain measured amounts of each compound, the intensity of the diffraction pattern of α-lead dioxide is weaker than it should be, relative to the known amount of this phase present. Federova, *et al.*,[58,59] attributed the abnormally low intensity to a coating-over of crystallites of α-lead dioxide by the softer β-lead dioxide during preparative grinding and mixing. Burbank, *et al.*,[5] suggests that it is possible that a recrystallization to the stable β-lead dioxide takes place in the superficial layers of the metastable crystals of α-lead dioxide, perhaps initiated by the presence of crystals of the stable phase in the mixtures. This mechanism, in the light of the findings of White, *et al.*,[53] who could not preserve the α structure upon quenching to room temperature and pressure in the presence of moisture, is interesting. Dickens[63] calculated the structure factors from the diffraction pattern, and these corresponded with structure factors derived for the α-lead dioxide structure proposed by Zaslavskii and Tolkachev.[45] Good agreement confirmed the random orientation of the sample prepared in this way and left little doubt that the different intensity ratios in the powder pattern of the electrodeposited samples were due to preferred orientation effects. The intensity ratios of the diffraction patterns from the powdered samples obtained by electrodeposition differed from those for the other samples. This suggested that the powder was packing in the holder in a nonrandom fashion. Changes in the intensity ratios when the samples were milled was further evidence that preferred orientation effects were present. When the samples obtained by the other methods were milled, the intensity ratios of their diffraction patterns showed no change, suggesting that these samples were completely randomly orientated.

Acton[64] has reported a method of making thin optically transparent sections of lead dioxide deposits which when examined with polarized light proved partially successful in distinguishing between α- and β-lead dioxide.

A number of descriptions for the chemical analysis of lead dioxide are given in the literature, and for examples the reader is referred to the papers of Bagshaw, *et al.*,[14] and Duisman and Giaque.[10]

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C. γ-LEAD DIOXIDE

The existence of a pseudo-tetragonal form (γ) has been suggested by a number of workers.[65-68] Perrault and Brenet[68] studied the decomposition of Pb_3O_4 in nitric acid and acetic acid. X-Ray, chemical, and thermogravimetric analyses indicated a second polymorph other than the normally expected β polymorph. As yet, further evidence for the existence of a γ form is awaited.

D. STABILITY AND INTERCONVERSION OF α- AND β-LEAD DIOXIDE

Under normal laboratory conditions β-lead dioxide is the more stable polymorph. However, under pressure β-lead dioxide may be transformed to α-lead dioxide.[53-59] A pressure of ~125,000 psig is required.[69] When the pressure was released, the β form did not reappear even after a year at room temperature.[53] However, at 100° some β-lead dioxide was detected after 2 weeks; at 290° lead dioxide begins to lose oxygen.[9,70] White, *et al.*,[53] record the heat of transition of α-lead dioxide to β as 11 cal/mol at 1 atm pressure and 32°. Burbank[71] reports that α-lead dioxide is converted to β-lead dioxide just before the β form is thermally decomposed and the conversion temperature lies between 296 and 301°. Thermogravimetric studies of α- and β-lead dioxide have been made by a number of workers.[72-77]

E. CONDUCTIVITY

Lead dioxide is highly conducting. Thomas[47] recorded the resistance of lead dioxide in a pellet form as 2×10^{-4} ohm cm and in compacted battery plate active material as 74×10^{-4} ohm cm in agreement with the earlier measurement of 0.95×10^{-4} ohm cm reported by Palmaer[78] for the microporous battery plate lead dioxide. Aguf, *et al.*,[79] determined the resistivity of both α- and β-lead dioxide as 10^{-3} and 4×10^{-3} ohm cm, respectively. Hall effect measurements carried out on lead dioxide samples[47,80] indicated a Hall coefficient of between -1.7 and -3.4×10^{-2} cm²/C, showing that the charge carriers are electrons. Carrier concentrations of from 10^{20} to 10^{21} electrons/cm³ were recorded.

Nuclear magnetic resonance (nmr) studies of lead dioxide have been reported[81-83] using ^{207}Pb. The value of +0.63 to +0.65% for the Knight shift (the Knight shift in lead dioxide resonance is dependent on the density of electrons at the top of the Fermi distribution[83] and is a qualitative measure of the conductivity of the sample) with respect to metallic lead showed that lead dioxide behaves as a metal in this respect. Piette and Weaver[81] concluded that this chemical shift for the magnetic resonances in lead dioxide is due to the conduction of electrons, because the lattice relaxation resonance time is short.

A number of workers[47,80,84] have suggested that the conductivity of lead dioxide is associated with the excess lead present in the nonstoichiometric compound. Conversely, Frey and Weaver[83] concluded that a deficiency of oxygen rather than impurity content of the sample is responsible for the conductivity of lead dioxide, for as oxygen is removed from lead dioxide, the Knight shift increases, showing a decrease in conductivity. Ruetschi and Cahan[84] point out that the reported[85] conductivity decreased as oxygen was removed from lead dioxide and that the Hall coefficient increased showing a decrease in the number of charge carriers. If the conductivity is caused by the deficiency of oxygen, the opposite effect should have been observed, although the stability range of lead dioxide with respect to oxygen content is very narrow before a change of phase sets in. The appearance of a poorly conducting phase in the partially reduced lead dioxide could well explain the loss of conductivity as oxygen is removed. Optical absorption measurements by Lappe[80] of thin films of lead dioxide (~100 Å thick) produced by sputtering Pb in an O_2–Ar atmosphere on quartz surfaces showed that, when the O_2 content was below 3%, the films were composed of pure Pb and, when between 3 and 25%, low conducting film of Pb_3O_4 was formed, but, when above 25%, a highly conducting film of lead dioxide was obtained containing both the tetragonal and orthorhombic modifications. It appeared from this work that lead dioxide is a highly doped semiconductor with excess Pb and a band width of about 1.5 eV.

In many cases the oxygen content of α-lead dioxide is less than that of β-lead dioxide; therefore, if oxygen deficiency is the cause of the conductivity of lead dioxide, the α form should be a slightly better electronic conductor than the β form. This conclusion is supported by the nmr measurements of Frey and Weaver[83] who report that the Knight shift for the α form is 0.48%, whereas the shift for the β form is 0.63% indicating that the conductivity of α-lead dioxide is slightly better than that of β-lead dioxide. Ruetschi and Cahan[69] have also suggested that free electrons in lead dioxide may be due in part to OH groups substituting for oxygen in the lattice. This is supported by analytical evidence of appreciable amounts of bound hydrogen in electrodeposited lead dioxide.[14,84,86-88] Hydrogen is known to play a similar

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role in other oxide semiconductors, *e.g.*, in ZnO.[89] The presence of hydrogen is not necessary to explain high electron concentrations as was shown in experiments with sputtered lead dioxide films by Lappe;[80] these films did not contain hydrogen and also had a carrier density of 10^{21} cm^{-3}. The influence of impurities other than hydrogen is small, since high concentrations are necessary to cause significant relative changes in the carrier concentration. It is for the same reason that doping of lead dioxide with 3- or 5-valent ions has little influence on the conductivity (*cf.*, SnO_2). Mindt[90] found it impossible to decide whether electrons in electrodeposited lead dioxide were due mainly to nonstoichiometry or to incorporation of hydrogen. The carrier concentration of 1.4×10^{21} cm^{-3} found in the α-lead dioxide films corresponded to a composition of $PbO_{1.971}$ if electrons are due only to ionized oxygen vacancies, and to $PbO_{1.942}(OH)_{0.058}$ if they are due only to OH groups substituting for oxygen. Chemical analytical methods are not sufficiently exact to distinguish between the two cases. In particular, the determination of hydrogen involves a large error,[14] and it is difficult to distinguish between hydrogen bound in OH groups in the lattice and hydrogen which is part of adsorbed water.

The decomposition of electrodeposited lead dioxide at room temperature can be interpreted in terms of the generation of oxygen vacancies or the incorporation of hydrogen due to oxidation of water. In both cases, oxygen was evolved and the electron concentration increased. The overall reaction is considered by Mindt[90] to be

$$(2O^{2-})_{latt} \longrightarrow (2\square O + 4e^-)_{latt} + (O_2)_{gas} \quad (1)$$

$$(4O^{2-})_{latt} + 2H_2O \longrightarrow (4OH^- + 4e^-)_{latt} + (O_2)_{gas} \quad (2)$$

where $\square O$ denotes an interstitial oxygen atom.

The result that moisture in the air increases the decomposition rate makes reaction 2 more probable although a similar effect may result if adsorbed water increases the rate of one step of reaction 1. The different electron mobilities in α- and β-lead dioxide are the result of several factors. The lower mobility in the α-lead dioxide films may be due in part to the smaller size of the crystallites in this modification. The average size of the α-lead dioxide crystallites is about 2000 Å, compared with 5000 Å for the β modification.[90] There is certainly also an influence of the higher carrier density in α-lead dioxide, since this corresponded to a larger number of lattice defects at which electrons are scattered. Since the α-lead dioxide films have a high degree of orientation (the (100) axis is perpendicular to the substrate), an anisotropy of the mobility in α-lead dioxide might also influence the results.

F. MORPHOLOGIES OF α- AND β-LEAD DIOXIDE

Prior to the detection by Kameyama and Fukumoto[42] of α-lead dioxide, it is clear that most of the previous studies of structure concern the β polymorph. Several examinations of the surface morphology of lead dioxide deposits have been made,[64,91-100] but in general the deposits concerned have been in the form of battery plates, for which it has been shown that the strength and durability of the plates depend markedly on the morphology of the crystal mass. Simon and Jones,[95,96] for example, showed that maximum lifespan was obtained for a lead dioxide lattice containing large euhedral crystals which they concluded were of α-lead dioxide. It has been shown that different methods of preparation produce different morphologies and crystallinities of α-lead dioxide.[14] A number of different preparations of α- and β-lead dioxide and positive active material from battery plates were examined by Kordes[60] using X-ray diffraction, small-angle scattering, and neutron diffraction. It was found that the interior of a battery plate was well crystllized, whereas the outer layers were less well crystallized. The small-angle scattering investigations showed that the shape factor for the lead dioxide particles was 1.2–1.3; however, it could not be determined whether they were of the form of rods or platelets. The average particle size was between 0.38 and 0.56 μ, from which the specific surface area was calculated as 15 and 24 m^2/g. Surface area determinations using gas absorption methods show lower values ($\sim$7 m^2/g).[41,60]

Mineral deposits of lead dioxide do not generally occur as well-developed crystals but occur in nodular masses. Synthetic crystals exhibit more crystallinity, but most preparations do not produce crystals large enough to be studied by optical methods. Astakhov, *et al.*,[94] examined electrodeposits of α- and β-lead dioxide and found that α-lead dioxide was deposited as a low surface area deposit of densely packed large crystals ($\sim$1 μ in diameter), whereas the β-lead dioxide formed a high surface area deposit of a porous mass of needles. Work by Burbank[98] has shown that the initial deposit of lead dioxide on pure lead by anodization in H_2SO_4 appeared to be prismatic, but thickening of the deposit caused the lead dioxide to lose the prismatic character and Feitknecht and Gaumann[101] have shown that the surface of cycled (alternately reduced to $PbSO_4$ and then reoxidized) lead dioxide becomes covered with nodular masses of lead dioxide. Burbank[98] determined the size of these particles as 0.1 μ in diameter which agreed with Feitknecht and Gaumann;[101] however, X-ray studies of Feitknecht[102] estimate the particle diameter to be $\sim$100 Å. The structure of battery plates immediately following oxidation in dilute H_2SO_4[103] indicated compound spikes of 0.5 μ crystals covered with a layer of sessile crystallites 0.1 μ or less in diameter together with rodlike crystallites or whiskers. During the course of charge and discharge,

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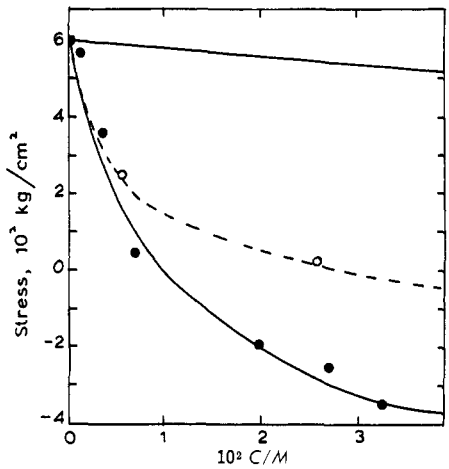

Figure 2. Effect of concentration of anions on stress in lead dioxide electrodeposits at 23°, 30 mA cm^{-2}, from ref 110 by permission of the *British Corrosion Journal*. Electrolyte, 1.21 *M* lead nitrate: (−) acetate, (●) tartrate; (○) citrate, added at concentration, *C*.

Kordes[60] has shown that crystal size increases to ~0.55–−0.6, but the shape factor is reduced to ~0.9, indicating a gradual crystal growth of the lead dioxide particles.

It is clear from work concerning the morphology of lead dioxide that both polymorphs are far from smooth.

G. MECHANICAL PROPERTIES

Bakhchisaraits'yan, *et al.*,[104] investigated a number of physicomechanical properties of lead dioxide including microhardness, brittleness, and internal stresses of lead dioxide films electrodeposited on nickel bases from alkaline plumbite electrolytes. These workers studied the relationship between the properties of lead dioxide and (a) the conditions of its formation, (b) the current density, and (c) the presence of organic additions in the electrolyte (ethylene glycol). It was observed that the introduction into the forming electrolyte of ethylene glycol, in concentrations above 4 *M*, leads to a fall in the microhardness, brittleness, and brilliance. With organic additive the internal stresses become compression stresses which reach a comparatively high value. For higher concentrations of additive an increase in current density also causes compression stresses in the deposit. In organic free electrolytes the properties of the deposit, apart from brilliance, depended upon current density to only a small extent. Bakhchisaraits'yan, *et al.*,[104] connected the changes in properties with the changes in microstructure and the composition of the deposits. The occurrence and growth of high internal compression stresses were particularly linked with changes in volume of the deposit[105–107] and with the lead oxide content in the deposit which increased with increasing ethylene glycol. In later papers Bakhchisaraits'yan, *et al.*,[108,109] reported investigations of the anodic stability of electrodeposited α-lead dioxide in some acid solutions. It was found that lead dioxide is fairly stable in nitric and perchloric acid solutions up to concentrations of 40–50%. Any stability was associated with the transformation of orthorhombic α-lead dioxide to tetragonal β-lead dioxide. In highly concentrated solutions of H_2SO_4, breakdown of electrodes was *ca.* three to four times higher than in nitric and perchloric acid, leading to the formation of salts of Pb(II) and Pb(IV). Stability increased with higher temperatures and in the presence of oxidizing agents. The increased breakdown in H_2SO_4 solutions was associated[108] with the presence of H_2O_2 (formed on electrolysis of H_2SO_4).

$$PbO_2 + H_2O_2 + 2H^+ \longrightarrow Pb(II) + O_2 + 2H_2O \quad (3)$$

For both nitric and perchloric acids no H_2O_2 is formed by electrolysis at the electrode.

Electrodeposits of lead dioxide are frequently stressed,[110–112] causing cracking and detachment of the deposit from the substrate and inferior discharge properties under galvanostatic conditions. The development of stress in electrodeposits (mainly metals) has been investigated,[113] and it is well known that the match/mismatch of the deposited lattice on the lattice of the substrate is not the only factor involved, although it may be important in certain cases. Bushrod and Hampson[110] investigated stress setup in lead dioxide electrodeposited from lead nitrate solutions and reported the presence of high compressive stress. At low Pb ion concentrations, the addition of acetate, citrate, and tartrate ions was investigated (Figure 2).

It was suggested that the adsorbed anions participated in the packing of the structural units that form the deposit. The greater the surface concentration of the adsorbed ion, the greater is the proportion of the electrode surface which cannot be used in the crystal growth process without displacing the adsorbate. A more open crystal structure then occurs, and the compressive stress is reduced and eventually reversed to become tensile as more adsorbate covers the surface. No change in the α:β ratio of the lead dioxide deposit was observed for varying deposit stress, indicating that the parameters which determine the α or β arrangement are more fundamental than those which determine the nature of the stress. Analysis of electrodeposits did not preclude the possibility of the presence of hydrogen and additional oxygen in the deposit giving rise to stresses. Hydrogen inclusion in the lattice could arise *via* a mechanism similar to that proposed[114] for the formation of lead dioxide.

$$Pb^{2+} + 2OH^- = Pb(OH)_2 \quad (4)$$

$$Pb(OH)_2 = Pb(OH)_2^{2+} + 2e \quad (5)$$

$$Pb(OH)_2^{2+} = PbO_2 + 2H^+ \quad (6)$$

The effect of very high current densities on the stress was considered complementary to the other observations, since at the higher positive potentials involved at higher current densities, the adsorption of anions would be favored. Shibas-

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aki[115] investigated the textures of electrodeposits of lead dioxide from $Pb(NO_3)_2$ solutions and its relation to strength and deposition conditions. Slightly coarse lead dioxide which was brittle and easily cracked was formed under low current density at normal temperatures. At lower current densities in the presence of certain impurities stronger, dull, smooth lead dioxide was obtained. The most suitable conditions for obtaining a strong bright form of lead dioxide were (a) smooth substrate surface, (b) low temperatures, (c) presence of one or more of Al^{3+}, Mn^{2+}, polyoxyethylenealkyl ether, *p*-toluenesulfonamide, (d) absence of iron and cobalt, (e) high concentration of Pb(II).

IV. Standard Electrode Potentials

A. GENERAL

The potential of the Pb|lead dioxide electrode which corresponds in acid solutions to

$$\beta\text{-}PbO_2 + 4H^+ + 4e \rightleftharpoons Pb + 2H_2O \quad (7)$$

was at 0.666 V (all potentials are referred to the standard hydrogen electrode) according to Lander[116] and at 0.665 V according to Ruetschi and Cahan.[69]

For the reaction

$$3\alpha\text{-}PbO_2 + 2H_2O + 2e \rightleftharpoons Pb_3O_4 + 4OH^- \quad (8)$$

E_0 was found to be 1.22 V in acid solution and 0.294 V in alkaline solution.[117]

The $PbO_2|PbSO_4$ reaction

$$PbO_2 + SO_4^{2-} + 4H^+ + 2e \rightleftharpoons PbSO_4 + 2H_2O \quad (9)$$

is of the most interest because of the commercial applications. Vosburgh and Craig[13] describe the construction of an electrode in which a paste is made in H_2SO_4 solution with about equal quantities of $PbSO_4$ and lead dioxide obtained from the electrolysis of a nitric acid solution of $Pb(NO_3)_2$. Electrical contact was made with a Pt wire, and the E_0 potential of the electrode corresponding to eq 9 at 25° was recorded by Vosburgh and Craig[13] as 1.681 V.

Hamer[12] considered that determinations of the potential of the lead dioxide|$PbSO_4$ electrode reported previous to 1935 were subject to errors because inferior reference electrodes had apparently been used. Using a $Pt|H_2$ reference electrode, the standard potential of the lead doxide|$PbSO_4$ electrode as a function of temperature (0–60°) is

$$E_0 = 1.67699 + 2.85 \times 10^{-4}T + 1.2467 \times 10^{-6}T^2 \quad (10)$$

At 25° E_0 = 1.68597 V.

Activities of H_2SO_4 and H_2O determined[118] from the emf data reported by Hamer[12] for a series of H_2SO_4 solutions and compared with the corresponding values calculated from vapor pressure measurements indicate a discrepancy of about 2 mV.[119,120] Beck and coworkers[121,122] considered that Hamer's[13] emf data are unreliable; the potential of the $PbO_2|PbSO_4$ electrode was studied over a range of H_2SO_4 concentrations from 0.1 to 8 molality and over a range of temperature from 5 to 55°. The results of Beck and coworkers[121,122] obey the Nernst relationship, and the temperature coefficient conforms to calorimetric data.[120] The activities obtained from Stokes' data[120] yield a constant value of 1.687 V for E_0[123] as determined[121,122] experimentally for E_0. The electrode system was reversible over the experimental range studied, and the lead dioxide|$PbSO_4$ electrode was found to be a good reference electrode as emphasized by Ives and Janz.[124] No easy explanation of the discrepancy is apparent. The data of Beck, *et al.*,[121,122] are shown in Table II.

Table II

Temperature Coefficient of Emf and Heat of Cell Reaction at 25°[a]

H_2SO_4, *m*	$-dE/dT \times 10^3$, $10^{-3}V\ °K^{-1}$	$-\Delta H$, *kcal*
0.1000	0.4320	78.156
0.1996	0.3967	78.490
0.2917	0.3721	78.604
0.4714	0.3290	78.604
1.129	0.2570	78.834
2.217	0.2122	79.485
3.900	0.2104	81.065
4.973	0.2314	82.309
6.095	0.2417	83.385
7.199	0.2512	84.397

[a] 1 cal ≡ 4.184 J

Bode and Voss[125] reported that the potential of lead dioxide|$PbSO_4$ was different for α-lead dioxide from that for β-lead dioxide. This difference in potential apparently amounted to ~30 mV, the β form having the more negative potential. Ruetschi and coworkers[84,126] found a potential of 1.7085 V for the α-lead dioxide|$PbSO_4$ electrode and 1.7015 V for the β-lead dioxide|$PbSO_4$ electrode with respect to a $Pt|H_2$ reference electrode at 25° in 4.4 *M* H_2SO_4. (Ruetschi and Cahan showed that although in acid solutions the α-lead dioxide electrode has a potential 7 mV above that of β-lead dioxide, there is a crossover in the pH region 1–2 where the β-lead dioxide electrode potential becomes more positive than that of α-lead dioxide.) E_0 values[127] of 1.698 V for α-lead dioxide and 1.690 V for β-lead dioxide are reported. From considerations of the physical and chemical properties of α- and β-lead dioxide,[84,126,127] the results obtained by Bode and Voss[125] are probably in error. Bone and coworkers[128] also found the potential of α-lead dioxide electrodes to be about 10 mV more positive than that of β-lead dioxide electrodes in confirmation of Ruetschi, *et al.*[127]

Duisman and Giaque[10] have studied the heat capacity of an electrolytic specially prepared sample of lead dioxide in the temperature range from 15 to 318°K. (The composition

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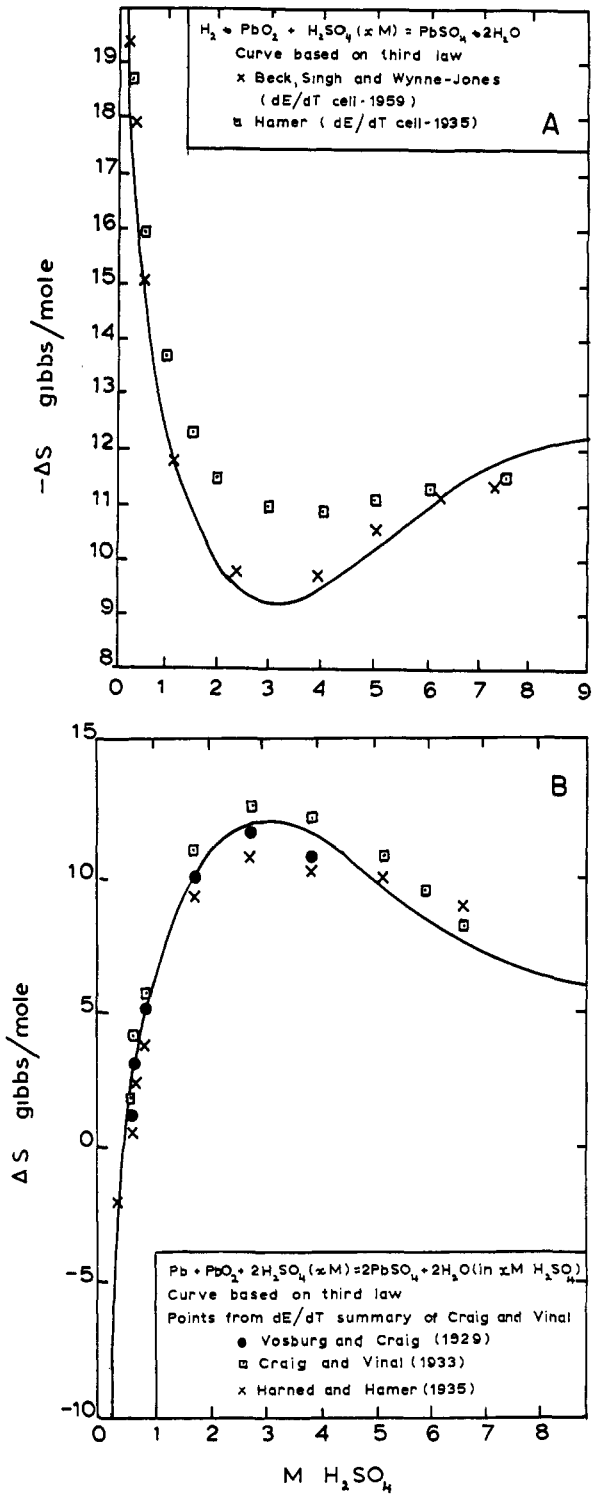
H₂ + PbO₂ + H₂SO₄ (x M) = PbSO₄ + 2H₂O
Curve based on third law
x Beck, Singh and Wynne-Jones (dE/dT cell-1959)
Hamer (dE/dT cell-1935)
A
-ΔS gibbs/mole
B
ΔS gibbs/mole
Pb + PbO₂ + 2H₂SO₄ (x M) = 2PbSO₄ + 2H₂O (in x M H₂SO₄)
Curve based on third law
Points from dE/dT summary of Craig and Vinal
Vosburg and Craig (1929)
Craig and Vinal (1933)
Harned and Hamer (1935)
M H₂SO₄

Figure 3. (A) Entropy change during reduction of PbO_2 by H_2 in x M H_2SO_4 from ref 10 by permissin of the American Chemical Society. (B) Entropy change in lead storage cell from ref 10 by permission of the American Chemical Society.

was PbO_2: 1.519×10^{-2} PbO: 2.558×10^{-2} H_2O). After correction for impurity content, the entropy of lead dioxide was 17.16 cal deg^{-1} mol^{-1} at 298.15°K. The entropy change in the cell reaction

$$H_2 + PbO_2 + H_2SO_4 = 2H_2O + PbSO_4 \quad (11)$$

Table III

	α-PbO_2	β-PbO_2
Free energy of formation, $\Delta G°$, per mol, kcal	−51.94	−52.34
Enthalpy of $\Delta H°$ formation, kcal	−63.52	−66.12
Entropy S, cal deg^{-1}		18.3
Heat capacity C_p, cal deg^{-1}		15.45

calculated from the third law of thermodynamics was in excellent agreement with the value dE/dT of Beck, Singh, and Wynne-Jones[129] and supports the use of third-law data on lead dioxide, Pb, $PbSO_4$, and H_2SO_4 (x M) to calculate the temperature coefficient of the lead storage cell. Duisman and Giaque[10] also computed values of the change of potential of the lead storage cell over the range 0–60° and from 0.1 to 14 M H_2SO_4 using the third law of thermodynamics. For the reaction

$$Pb + PbO_2 + 2H_2SO_4 \text{ (pure)} = 2PbSO_4 + 2H_2O \text{ (pure)} \quad (12)$$

$\Delta G° = -120{,}200$ cal/mol and $\Delta H° = -121{,}160$ cal/mol at 298.15°K.

The entropy data for the lead dioxide electrode referred to the standard hydrogen electrode and also in conjunction with the lead electrode in sulfuric acid (the most important applications) are shown in Figure 3. Duisman and Giaque[10] have presented a large amount of detailed information regarding the thermodynamic data of lead dioxide. An abstract of such thermodynamic data is given in Table III.

B. POURBAIX DIAGRAMS

Delahay, *et al.*,[117] have constructed a potential–pH diagram[130] for lead in the presence of sulfate ions. This has been extended by Reutschi, *et al.*,[39] Barnes and Mathieson,[131] and Ness[2] to include the basic lead sulfates. By using the data of Bode and Voss[125] a potential–pH diagram was constructed showing the ranges of thermodynamic stability of the materials of interest: Pb, PbO, Pb_3O_4, lead dioxide, $PbSO_4$, $PbO \cdot PbSO_4$, and $3PbO \cdot PbSO_4 \cdot H_2O$. Diabasic and tetrabasic lead sulfates were considered.

Figure 4 shows the potential–pH diagram of lead, in aqueous solutions containing a total sulfate ion activity ($a_{SO_4^{-2}} + a_{HSO_4^-}$) equal to 1 g-ion /l., constructed by Barnes and Mathieson.[131]

1. *Notes to Diagram (with the authors'[131] permisson)*

Thermodynamic Formulas. Following Barnes, *et al.*,[131] the potential E for the equilibrium ox + mH$^+$ + ne = y(red) + zH$_2$O at 25° is given by

$$E = \frac{G°_{ox} - yG°_{red} - zG°_{H_2O}}{23{,}070n} - 0.0591\frac{m}{n}\text{pH} + \frac{0.0591}{n}\log\frac{a_{ox}}{a^y_{red}}$$

(129) W. H. Beck, K. P. Singh, and W. F. K. Wynne-Jones, *Trans. Faraday Soc.*, **55**, 331 (1959).
(130) M. Pourbaix, "Atlas of Electrochemical Equilibrium," Gauthiers-Villars, Paris, 1963.
(131) S. C. Barnes and R. T. Mathieson, in ref 95, p 41.

Table IV

Compd	$G°$, *cal*	*Compd*	$G°$, *cal*
H_2O	−56,690	$3PbO \cdot PbSO_4 \cdot H_2O$	−397,300
Pb	0	Pb^{2+}	−5,810
PbO	−45,250	$HPbO_2^-$	−81,000
Pb_3O_4	−147,600	Pb^{4+}	72,300
PbO_2	−50,860	PbO_3^{2-}	−66,340
$PbSO_4$	−192,532	SO_4^{2-}	−177,340
$PbO \cdot PbSO_4$	−243,200	HSO_4^-	−179,940

where $G°$ = standard free energy of formation of the reactants and a = activity of the reactants. The equilibrium constant K for the reaction $pA + mH^+ = qB + zH_2O$ is given by

$$\log K = \frac{pG°_A - qG°_B - zG°_{H_2O}}{2.3RT}$$

Standard Free Energies of Formation. All values were taken from Pourbaix[117,130] except those for the basic sulfate which were taken from Bode and Voss[125] (see Table IV).

2. Reactions

(a) $2H^+ + 2e = H_2$

$$E = -0.0591\text{pH} - 0.0295 \log p_{H_2}$$

(b) $O_2 + 4H^+ + 4e = 2H_2O$

$$E = 1.228 - 0.0591\text{pH} + 0.0147 \log p_{O_2}$$

(c) $SO_4^{2-} + H^+ = HSO_4^-$

$$\log \frac{a_{HSO_4^-}}{a_{SO_4^{2-}}} = -1.92 + \text{pH}$$

(d) $Pb^{2+} + 2H_2O = HPbO_2^- + 3H^+$

$$\log \frac{a_{HPbO_2^-}}{a_{Pb^{2+}}} = -28.02 + 3\text{pH}$$

(e) $Pb^{4+} + 3H_2O = PbO_3^{2-} + 6H^+$

$$\log \frac{a_{PbO_3^{2-}}}{a_{Pb^{4+}}} = -23.06 + 6\text{pH}$$

(f) $Pb^{2+} = Pb^{4+} + 2e$

$$E = 1.694 + 0.0295 \log \frac{a_{Pb^{4+}}}{a_{Pb^{2+}}}$$

(g) $Pb^{2+} + 2H_2O = PbO_3^{2-} + 6H^+ + 2e$

$$E = 2.375 - 0.1771\text{pH} + 0.0295 \log \frac{a_{PbO_3^{2+}}}{a_{Pb^{2+}}}$$

(h) $HPbO_2^- + H_2O = PbO_3^{2-} + 3H^+ + 2e$

$$E = 1.547 - 0.0886\text{pH} + 0.0295 \log \frac{a_{PbO_3^{2-}}}{a_{HPbO_2^-}}$$

3. Limits of Domains of Predominance of Soluble Lead Ions

(d′) $Pb^{2+}/HPbO_2^-$

$$\text{pH} = 9.34$$

(e′) Pb^{4+}/PbO_3^{2-}

$$\text{pH} = 3.84$$

(f′) Pb^{2+}/Pb^{4+}

$$E = 1.694$$

(g′) Pb^{2+}/PbO_3^{2-}

$$E = 2.375 - 0.1773\text{pH}$$

(h′) $HPbO_2^-/PbO_3^{2-}$

$$E = 1.547 - 0.0886\text{pH}$$

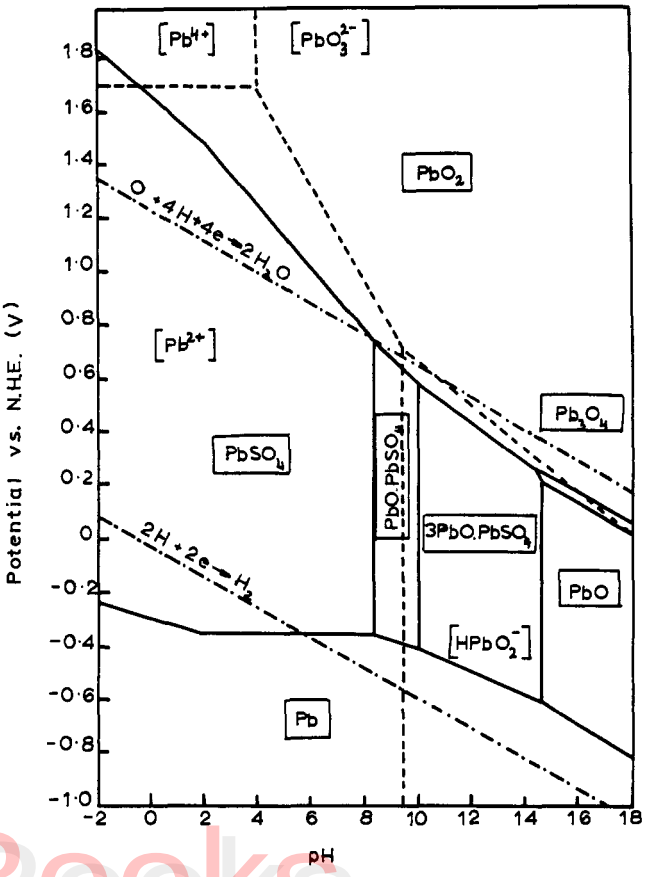

Figure 4. Potential–pH diagram of lead in the presence of sulfate ions at unit activity and 25° from ref 131 by permission of Pergamon Press.

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4. Limits of Domains of Stability of Two Phases without Oxidation

(i) $4PbO + SO_4^{2-} + 2H^+ = 3PbO \cdot PbSO_4 \cdot H_2O$

$$\text{pH} = 14.6 + {}^1/_2 \log a_{SO_4^{2-}}$$

(j) $3PbO \cdot PbSO_4 \cdot H_2O + SO_4^{2-} + 2H^+ = 2(PbO \cdot PbSO_4) + 2H_2O$

$$\text{pH} = 9.6 + {}^1/_2 \log a_{SO_4^{2-}}$$

(k) $PbO \cdot PbSO_4 + SO_4^{2-} + 2H^+ = 2PbSO_4 + H_2O$

$$\text{pH} = 8.4 + {}^1/_2 \log a_{SO_4^{2-}}$$

5. Limits of Domains of Stability of Two Solid Phases with Oxidation

(l) $PbSO_4 + H^+ + 2e = Pb + HSO_4^-$

$$E = -0.300 - 0.0295\text{pH} - 0.0295 \log a_{HSO_4^-}$$

(m) $PbSO_4 + 2e = Pb + SO_4^{2-}$

$$E = -0.356 - 0.0295 \log a_{SO_4^{2-}}$$

(n) $PbO \cdot PbSO_4 + 4e + 2H^+ = 2Pb + SO_4^{2-} + H_2O$

$$E = -0.113 - 0.0295\text{pH} - 0.0148 \log a_{SO_4^{2-}}$$

(o) $3PbO \cdot PbSO_4 \cdot H_2O + 8e + 6H^+ = 4Pb + SO_4^{2-} + 4H_2O$

$$E = 0.030 - 0.044\text{pH} - 0.0074 \log a_{SO_4^{2-}}$$

(p) $PbO + 2e + 2H^+ = Pb + H_2O$

$$E = 0.248 - 0.0591\text{pH}$$

(q) $PbO_2 + HSO_4^- + 2e + 3H^+ = PbSO_4 + 2H_2O$

$$E = 1.655 - 0.0886\text{pH} + 0.0295 \log a_{HSO_4^-}$$

(r) $PbO_2 + SO_4^{2-} + 4H^+ + 4e = PbSO_4 + 2H_2O$

$$E = 1.687 - 0.1182\text{pH} + 0.0295 \log a_{SO_4^{2-}}$$

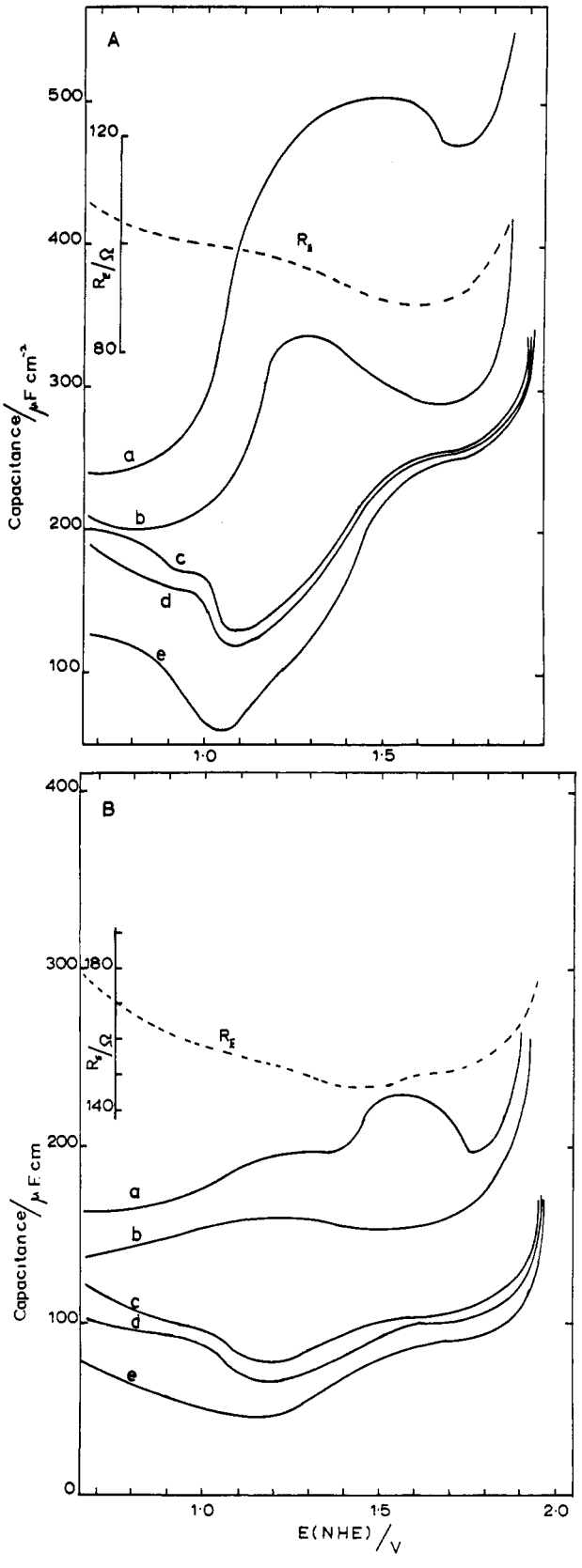

Figure 5. Differential capacitance *vs.* bias potential curves for electrodeposited α-lead dioxide (A) and β-lead dioxide (B) in aqueous KNO_3 solutions, at 23°, 120 Hz: (a) 0.307 *M*; (b) 0.115 *M*; (c) 0.018 *M*; (d) 0.0121 *M*; (e) 0.0043 *M*. Broken line shows the electrode resistance, R_E, *vs.* potential curve at 23°; electrode area 4.49×10^{-2} cm², 0.307 *M* aqueous KNO_3, 120 Hz, pH 5.7. From ref 138 by permission of the *Journal of Electroanalytical Chemistry*.

(s) $2PbO_2 + SO_4^{2-} + 4e + 6H^+ = PbO \cdot PbSO_4 + 3H_2O$
$E = 1.468 - 0.0886pH + 0.0148 \log a_{SO_4^{2-}}$

(t) $4PbO_2 + SO_4^{2-} + 8e + 10H^+ = 3PbO \cdot PbSO_4 \cdot H_2O + 4H_2O$
$E = 1.325 - 0.0739pH + 0.0074 \log a_{SO_4^{2-}}$

(u) $PbO_2 + 2e + 2H^+ = PbO + H_2O$
$E = 1.107 - 0.0591pH$

(v) $3PbO_2 + 4e + 4H^+ = Pb_3O_4 + 2H_2O$
$E = 1.122 - 0.0591pH$

(w) $Pb_3O_4 + 2e + 2H^+ = 3PbO + H_2O$
$E = 1.076 - 0.0591pH$

(x) $4Pb_3O_4 + 3SO_4^{2-} + 8e + 14H^+ = 3(3PbO \cdot PbSO_4 \cdot H_2O) + 4H_2O$
$E = 1.730 - 0.1034pH + 0.0074 \log a_{SO_4^{2-}}$

V. Structure of the Lead Dioxide–Aqueous Solution Interface

Studies of the double layer structure have been limited.[132-145] Kabanov, *et al.*,[132] made measurements using an electrode obtained by the anodic deposition of lead dioxide on a gold base from $Pb(NO_3)_2$ solution in H_2SO_4 (0.001–0.1 *N*) and $HClO_4$ (0.01 *N*) solution. These workers estimated the potential of zero charge (pzc) from a minimum in the capacitance curves (and from the presence of an inflection in the overpotential–log *i* curve) at 1.80 V and concluded that the diffuse double layer theory could be applied to lead dioxide electrodes. Displacement of the capacitance minimum with time was thought to be due to slow adsorption of electroactive species. From the observed capacitance and resistance change with time it was concluded that lead dioxide undergoes some process of surface modification. Kabanov[133,134] reported H_2SO_4 adsorption at the lead dioxide surface of accumulator positive electrodes and lead dioxide covered lead ribbon formed in H_2SO_4. It was concluded that H_2SO_4 was specifically adsorbed at positive surface charges, the extent of the adsorption depending upon the electrode potential. Evidence was presented that adsorbed H_2SO_4 accelerated the oxygen evolution reaction (oer). Leikis and Venstrem[135,136] measured the hardness of lead dioxide electrodes produced anodically from pure lead in H_2SO_4. From the maximum in the hardness–potential curve, the pzc was estimated to be 1.9 V in 0.05 *M* H_2SO_4 and 1.7 V in 2.5 *M* H_2SO_4. From the sharper decrease in hardness with potential, at potentials positive with respect to the pzc (rational poten-

(132) B. N. Kabanov, I. G. Kiseleva, and D. I. Leikis, *Dokl. Akad. Nauk SSSR*, **99**, 805 (1954).
(133) B. N. Kabanov, Proceedings of the Electrochemical Conference, Warsaw, 1957, p 515.
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(135) D. I. Leikis and E. K. Venstrem, *Dokl. Akad. Nauk SSSR*, **112**, 17 (1957).
(136) D. I. Leikis and E. K. Venstrem, *ibid.*, **112**, 97 (1957).
(137) G. A. Kokarev, N. G. Bakhchisaraits'yan, and G. J. Medvedev, *Katal. Reakts. Zhidk. Faze, Tr. Vses. Konf., 2nd, 1966*, 405 (1967).
(138) J. P. Carr, N. A. Hampson, and R. Taylor, *J. Electroanal. Chem.*, **27**, 109 (1970).
(139) J. P. Carr, N. A. Hampson, and R. Taylor, *ibid.*, **27**, 201 (1970).
(140) J. P. Carr, N. A. Hampson, and R. Taylor, *ibid.*, **28**, 65 (1970).
(141) J. P. Carr, N. A. Hampson, and R. Taylor, *ibid.*, **27**, 466 (1970).
(142) J. P. Carr and N. A. Hampson, *J. Electrochem. Soc.*, **118**, 1262 (1971).
(143) Ya. M. Kolotyrkin and G. J. Medvedev, *Zh. Fiz. Khim.*, **25**, 1355 (1951).
(144) F. J. Kukoz and S. A. Semenchenko, *Electrokhimiya*, **2**, 74 (1966); **1**, 1454 (1965).
(145) G. A. Kokarev, N. G. Bakhchisaraits'yan, A. N. Smirnova, and G. J. Medvedev, *Tr. Mosk. Khim. Tekhnol. Inst.*, **54**, 169 (1967).

tial), it was concluded that specific adsorption of sulfuric acid occurred at positive surface charges in agreement with Kabanov.[133,134] Kokarev, *et al.*,[137] have formulated equivalent electrical circuits for the impedance of the lead dioxide–0.005 *M* H_2SO_4 solution interphase in the presence and absence of isobutyl alcohol. They estimated the pzc from the adsorption of the alcohol, which occurred in the very narrow potential range 1.7–1.9 V, at 1.8 V. Complementary to these, studies of the interphase between α- and β-lead dioxide, supported on platinum bases, in a range of aqueous electrolyte solutions have recently been reported.[138–142] Measurements are presented for KNO_3, $NaClO_4$, phosphates, sulfates, and sodium hydroxide, the simplest system being KNO_3. In KNO_3 solutions[138] the time-stability of the impedance data indicated no development of the surface with time of electrode–electrolyte contact. The differential capacitance curves (Figure 5) resembled in shape those for mercury in sodium fluoride solution.[146] However, the potential region in the present case was about 1.5 V more positive than for the case of mercury. In the most concentrated electrolyte, a well-defined hump was obtained which, on dilution, became a pronounced hollow. From the magnitude of the capacitance it was suggested that the roughness factor for the lead dioxide electrodes was about 5–10 times that for mercury. Such a high value of roughness factor is in agreement with the observed frequency dispersion of the capacitance. The measurements showed that the capacitance minimum was not dependent upon electrolyte concentration, and hence the potential corresponding to the minimum was taken as the point of zero charge E_z. The value of E_z is 1.06 ± 0.01 V for α-lead dioxide and 1.15 ± 0.01 V for β-lead dioxide.

At all potentials the capacitance was less for β-lead dioxide than for α-lead dioxide. The capacitance curves shown in Figure 5 were integrated to give the surface charge on the electrode. At constant charge density the effect of concentration changes on the differential capacitance curves theoretically follows from eq 13. Using the connection between surface excess of adsorbed ions, $\Gamma_\pm$, electrode potential, $E_\pm$, measured with an electrode reversible to cation or anion, and charge on the electrode, q

$$\left(\frac{\partial E_\pm}{\partial \mu}\right)_q = -\left(\frac{\partial \Gamma_\pm}{\partial q}\right)_\mu \tag{13}$$

Since

$$\Gamma_\pm = q_\pm/z_\pm F,\ \partial\mu = -RT\,\partial \log a \tag{14}$$

and

$$E_R = E_\pm + (RT/z_\pm F) \ln a \tag{15}$$

$$\left(\frac{\partial E_\pm}{\partial \ln a}\right)_q = -\frac{RT}{z_\pm F}\left(\frac{\partial q_\pm}{\partial q}\right)_a \tag{16}$$

and for KNO_3 solution

$$\left(\frac{\partial E_R}{\partial \ln a}\right)_q = -\frac{RT}{F}\left\{\left(\frac{\partial q_\pm}{\partial q}\right)_a \pm \frac{1}{2}\right\} \tag{17}$$

Limiting values of $(\partial q_+/\partial q)_a$ and $(\partial q_-/\partial q)_a$ follow from the Gouy–Chapman theory[147,148]

	$(\partial q_+/\partial q)_a$	$(\partial q_-/\partial q)_a$
High positive q	0	−1
Zero q	−½	−½
High negative q	−1	0

It followed that values of $(\partial E_R/(RT/F)\partial \log a)_q$ at high positive, zero, and high negative charge were 1, 0, and −1, respectively.

Figure 6 shows potential, referred to the pzc, E_z, as a function of activity, expressed as (RT/F) ln a, indicating that specific adsorption is absent. Some divergence from the behavior observed in the case of mercury and expected from the Gouy–Chapman[147,148] theory was apparent. In particular, the magnitude of the surface charge corresponding to the various slopes of the E − log a lines is much less than the reported surface charge densities. This apparently arose as the Gouy–Chapman treatment assumes a smooth uniform electrode whereas lead dioxide is rough. At the higher electrode charge densities the magnitudes of the slopes increased. However, it has been pointed out by Delahay[149] that even for the mercury electrode at high charge density, deviations occur due to both defects in the Gouy–Chapman theory and because the contribution of the diffuse layer is relatively minor. The symmetry of the family of curves and the satisfactory slopes not far removed from E_z was taken as support for the correct choice of E_z. It was reported that in other electrolyte solutions the double layer was complicated by adsorption. In sulfate electrolytes,[139] for example, the capacitance curves were strongly influenced by pH. Figure 7 shows the results obtained. It was reported that the magnitude of the electrode capacitance rose progressively as pH was decreased. This, it was argued, indicated the participation of the H^+ ion in adsorption at the interphase. It was considered that at a high positive rational potential the direct adsorption of H^+ ion in the experimentally polarizable region was unlikely. The SO_4^{2-} ion, however, was expected to be adsorbed in view of the low solubility of $PbSO_4$. As the pH was lowered the concentration of HSO_4^- at the electrode was increased, and it was suggested that the observed pseudo-capacitance arose from reactions of the type

$$H^+ + SO_4^{2-}{}_{ads} = HSO_4^-{}_{ads} \tag{18}$$

$$4HSO_4^-{}_{ads} + PbO_2 + 2e = PbSO_{4,ads} + 3SO_4^{2-}{}_{ads} + H_2O \tag{19}$$

In the case of KNO_3 reactions of the type 19 were not possible.

The difference between the behavior of α- and β-lead dioxide electrodes in sulfate electrolytes was found to be marginal; however, in nitrate electrolytes the differences were significant. It was concluded that the adsorption of sulfate and surface reactions of type 19 obscured surface structural differences between the polymorphs. Similar reactions between adsorbed species were indicated for the lead dioxide–aqueous phosphate solution interphase.[140] Here, as with sulfate,[139] the magnitude of the electrode capacitance within the polarizable region was considerably greater than those observed for the nitrate system at equivalent concentrations. Further, the magnitude of the phosphate capacitances decreased progressively in the series H_3PO_4–KH_2PO_4–K_2HPO_4 and indicated the participation of the H^+ ion in the processes at the interphase. The direct adsorption of the H^+ ions at the positive rational potentials was unlikely; however, owing to the low solubility of the lead phosphates, it was considered feasible that PO_4^{3-},

(146) D. C. Grahame, *J. Amer. Chem. Soc.*, **76**, 4819 (1954).
(147) G. Gouy, *J. Phys. Radium*, **9**, 457 (1910); *C. R. Acad. Sci.*, **149**, 654 (1910).
(148) D. L. Chapman, *Phil. Mag.*, **25**, 475 (1913).
(149) P. Delahay, "Double Layer and Electrode Kinetics," Interscience, New York, N. Y., 1965, Chapter 2.

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HPO_4^{2-}, and $H_2PO_4^-$ ions were directly adsorbed according to reactions of the type

$$PbO_2 + 2H_2PO_{4,ads} + 2e = PbHPO_{4,ads} + HPO_4^{2-}{}_{ads} + 2H_2O \quad (20)$$

$$PbO_2 + 4H_2PO_4^-{}_{ads} + 2e = PbHPO_{4,ads} + 3HPO_4^{2-}{}_{ads} + 2H_2O \quad (21)$$

$$PbO_2 + 5HPO_4^{2-}{}_{ads} + 2e = PbHPO_{4,ads} + HPO_4^{3-}{}_{ads} \quad (22)$$

Such reactions are favored by decreasing the pH of the electrolyte; thus the lower pH resulted in a greater adsorption capacitance. Both phosphate and sulfate electrolytes have been used for accumulator electrolytes. The significant difference reported between the behavior of the lead dioxide|SO_4^{2-}, H^+ system and the lead dioxide|PO_4^{3-}, H^+ system was that potential excursions beyond the negative limit of the polarizable region resulted in a pronounced reduction in electrode capacitance in the sulfate system, apparently in accord with the flat capacitor formula. For both systems the appreciable faradaic current flow at such potentials indicated lattice reduction, and it was suggested that the particular lead(II) phosphate produced under these conditions had sufficient solubility to leave the electrode. Alternatively, it was considered that any lead phosphate film formed was only poorly adherent to the electrode and unable to act as a dielectric.

In NaOH[142] a minimum in the capacitance curves was observed at 1.15 V for β-lead dioxide; however, for α-lead dioxide the capacitance curves were much flatter, showing no pronounced minimum.

VI. Exchange Reactions

The dissolution, deposition, and exchange reactions at lead dioxide electrodes occur between species in the electrode surface and reduced particles on the solution side of the double layer. In certain systems where the Pb(II) ion is very insoluble, such as the $PbO_2|PbSO_4$, H_2SO_4 system, the situation may be more complex, owing to adsorption, than in systems where the Pb(II) ion is soluble since in the latter case the Pb(II) ion concentration can be determined. These simpler systems will be considered first.

A. ELECTRODE REACTIONS IN ALKALINE SOLUTIONS

The electrochemical behavior of lead dioxide in alkali was investigated by Carr, Hampson, and Taylor.[150] Galvanostatic experiments were reported for α-lead dioxide and β-lead dioxide deposited onto platinum bases. Overpotential–current density data were obtained corresponding to electrolytes based on 3 *M* total equivalent univalent salt concentration with added KNO_3. The reaction was reported to be slow ($i_0 \sim 0.1$ mA cm^{-2}). In one series [Pb(II)] was varied at constant [OH^-] and in the second [OH^-] was varied at constant [Pb(II)]. Measurements were made in the temperature range 0–66°. It was reported that in alkaline solutions free from Pb(II), β-lead dioxide electrodes were stable; for example, differential capacitance determinations[142] indicated a constant electrode capacitance for at least 24 hr after the initial electrode–electrolyte contact with 1 *M* KOH. In alkaline electrolytes containing Pb(II), it was reported[150] that β-lead dioxide electrodes progressively deteriorated, mechanical strength and adhesion were affected, and the deposit was disintegrated. It was not found possible to obtain reliable kinetic measurements on β-lead dioxide in alkaline electrolytes containing Pb(II). For α-lead dioxide, electrodes were stable. From the kinetic measurements and the concentration dependencies of both faradaic and exchange current densities, the following sequence was suggested for the electrode reaction

$$PbO_2 + H_2O + 2e = PbO_{ads} + 2OH^- \quad (23)$$

$$PbO_{ads} = PbO_{aq} \quad (24)$$

$$PbO_{aq} + OH^- + H_2O = Pb(OH)_3^- \quad (25)$$

where PbO_{ads} and PbO_{aq} represented respectively PbO adsorbed at the interphase and in solution. The potential–current density curves could be interpreted in terms of a transition of the charge-transfer reaction from an effective one-step process at low overpotential to two consecutive one-electron transfers at high overpotentials. This is similar to the behavior observed for lead dioxide electrodes in perchlorate electrolytes.[155–157] The mechanism of the lead dioxide|Pb(II) exchange in acid electrolytes in which Pb(II) is uncomplexed was reported to differ from that observed in alkali, for whereas the reduction in acid involved an initial addition of two H^+ ions to the lead dioxide, *viz.*

$$PbO_2 + 2H^+ = PbO_2(H^+)_2 \quad (26)$$

in alkali the initial step is the addition of a molecule of H_2O to the electrode. It was considered that the difference was not surprising in view of the very different potentials involved.

B. ELECTRODE REACTIONS IN PERCHLORATE SOLUTIONS

Mark and Vosburgh[151–153] investigated the discharge of lead dioxide electrodes, electrodeposited on a gold basis, in 0.15 *M* $HClO_4$ + 0.1 *M* $Pb(ClO_4)_2$ and obtained overpotential data which indicated that the exchange reaction was slow ($i_0 \sim 0.01$ mA cm^{-2}). In 1.0 *M* $HClO_4$ + 0.1 *M* $Pb(ClO_4)_2$ the exchange current was ~0.4 mA cm^{-2}. β-Lead dioxide electrodes were investigated by Jones, *et al.*[154] It was shown for the cathodic (discharge) reaction that before passivation the electrode remained free of films based on Pb(II). Measurements in the low overpotential region for β-lead dioxide, where the maximum potential excursion was limited to ±10 mV about the equilibrium potential, were made.[155] The charge-transfer reaction was slow. The dependence of the exchange current on the concentration of Pb(II) indicated a charge-transfer coefficient of 0.2 which was verified by an arithmetical analysis of current–potential data. Application of the order of reaction method to a study of the mechanism of exchange between β-lead dioxide and plumbous ions at high overpotentials in solution was investigated using a galvanostatic technique.[156] Interpretation of the charge-transfer overpoten-

(150) J. P. Carr, N. A. Hampson, and R. Taylor, *Ber. Bunsenges. Phys. Chem.*, **74**, 557 (1970).

(151) H. B. Mark, *J. Electrochem. Soc.*, **109**, 634 (1962).

(152) H. B. Mark, *ibid.*, **110**, 945 (1963).

(153) H. B, Mark and W. C. Vosburgh, *ibid.*, **108**, 615 (1961).

(154) N. A. Hampson, P. C. Jones, and R. F. Phillips, *Can. J. Chem.*, **45**, 2039 (1967).

(155) N. A. Hampson, P. C. Jones, and R. F. Phillips, *ibid.*, **45**, 2045 (1967).

(156) N. A. Hampson, P. C. Jones, and R. F. Phillips, *ibid.*, **46**, 1325 (1968).

Table V

Solution	kJ/mol α-PbO_2	kJ/mol β-PbO_2	Ref
0.025 *M* [Pb(II)], 3 *M* [H^+], Total [ClO_4^-] 6.85 *M*	12.6 (low temp) 42 (high temp)		157
0.09 *M* [Pb(II)], 0.5 *M* [H^+], Total [ClO_4^-] 6.85 *M*		31.1	155
0.039 *M* [Pb(II)], 0.68 *M* [OH], Total molar strength, 3 *M*	8.2 (low temp) 39.9 (high temp)		150

tial (η_D) *vs. i* data was consistent with a change in mechanism from a single two-electron-transfer step to two successive single-electron-transfer steps as the magnitude of the potential excursion from equilibrium was increased. Analysis of the slopes obtained from the linear logarithmic region indicated that the slow step in the reaction is that leading to the formation of a Pb(II) intermediate. The following mechanism was suggested on the basis of the kinetic data.

$$PbO_2 + 2H^+ \longrightarrow PbO_2(H^+)_{2,ads} \quad (27)$$

$$PbO_2(H^+)_{2,ads} + e = [HO\cdot Pb\cdot OH]^+ \quad (28)$$

$$HO\cdot Pb\cdot OH^+ + e = Pb(OH)_2 \quad (29)$$

$$Pb(OH)_2 + 2H^+ \longrightarrow Pb^{2+} + 2H_2O \quad (30)$$

In a later paper the cathodic passivation and the exchange reactions at α-lead dioxide in acid perchlorate electrolytes were reported using the galvanostatic technique.[157] The results were generally closely similar to those previously reported for β-lead dioxide, but some differences occur, and these were explained in terms of an α-/β-lead dioxide equilibration process. The most significant difference reported for α- and β-lead dioxide was in the order of reaction curves shown in Figures 8 and 9. The cathodic data for the log *i–E* variation in the case of β-lead dioxide all lay on the same line, whereas for α-lead dioxide they formed a parallel closely spaced set of lines. The data were interpreted as due to α-lead dioxide being unstable in acid environments and undergoing a change-over to β-lead dioxide because of the exchange reaction occurring at equilibrium.

C. ELECTRODE REACTIONS IN NITRATE SOLUTIONS

Mark[158] has studied the discharge of lead dioxide in nitrate electrolytes and compared the results with other soluble lead(II) systems. It appears from the results that the behavior is similar to the behavior in perchlorate electrolytes, although no kinetic constants (or reaction orders) other than exchange current density were evaluated.

D. TEMPERATURE DEPENDENCE OF EXCHANGE CURRENT DENSITIES

The data reported concerning the temperature dependence of the exchange current are scanty;[150,155,157] however, it is clear from Table V that the values fall at ~31 kJ/mol for

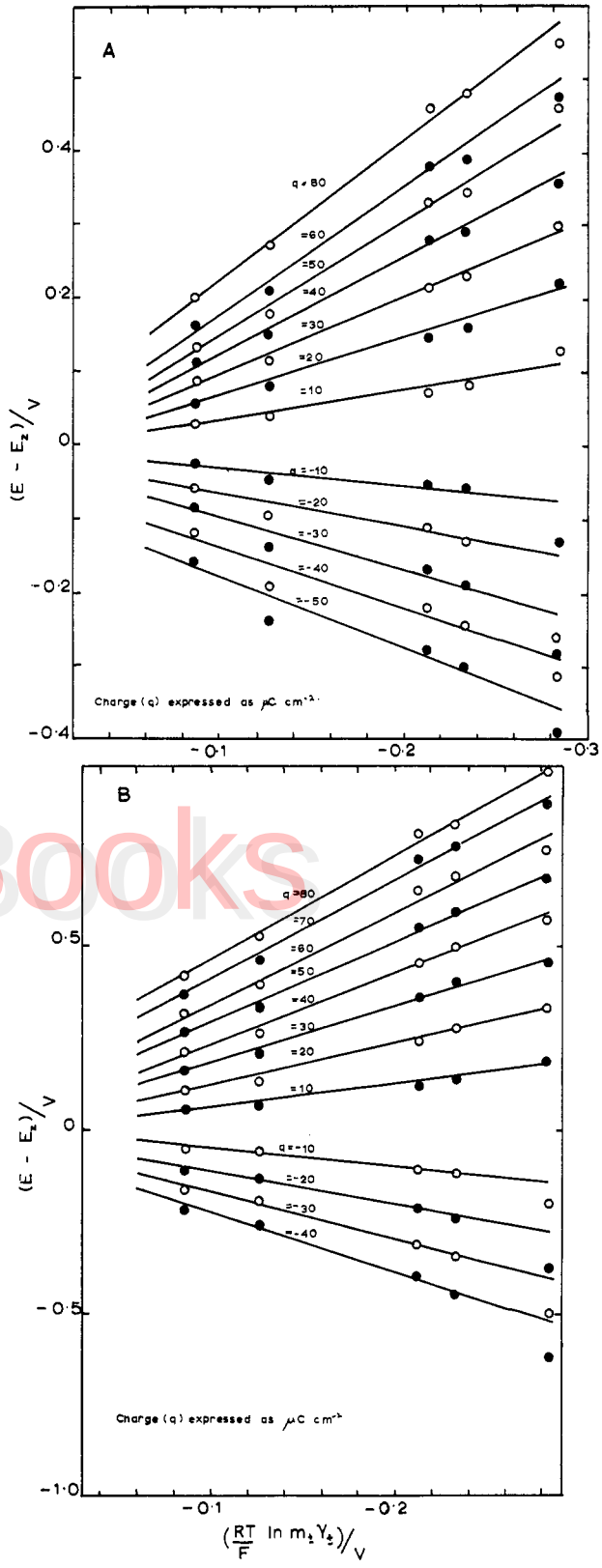

Figure 6. (A) Potential, referred to E_z, as a function of activity (RT/F ln $a_\pm$) for electrodeposited α-lead dioxide (A) and β-lead dioxide (B) at constant charge. From ref 138 by permission of the *Journal of Electroanalytical Chemistry*.

β-lead dioxide. In the case of α-lead dioxide the Arrhenius plot shows two distinct linear regions both for the exchange in alkali and acid perchlorate solutions. This break occurs at

(157) N. A. Hampson, P. C. Jones, and R. F. Phillips, *Can. J. Chem.*, 47, 2171 (1969).

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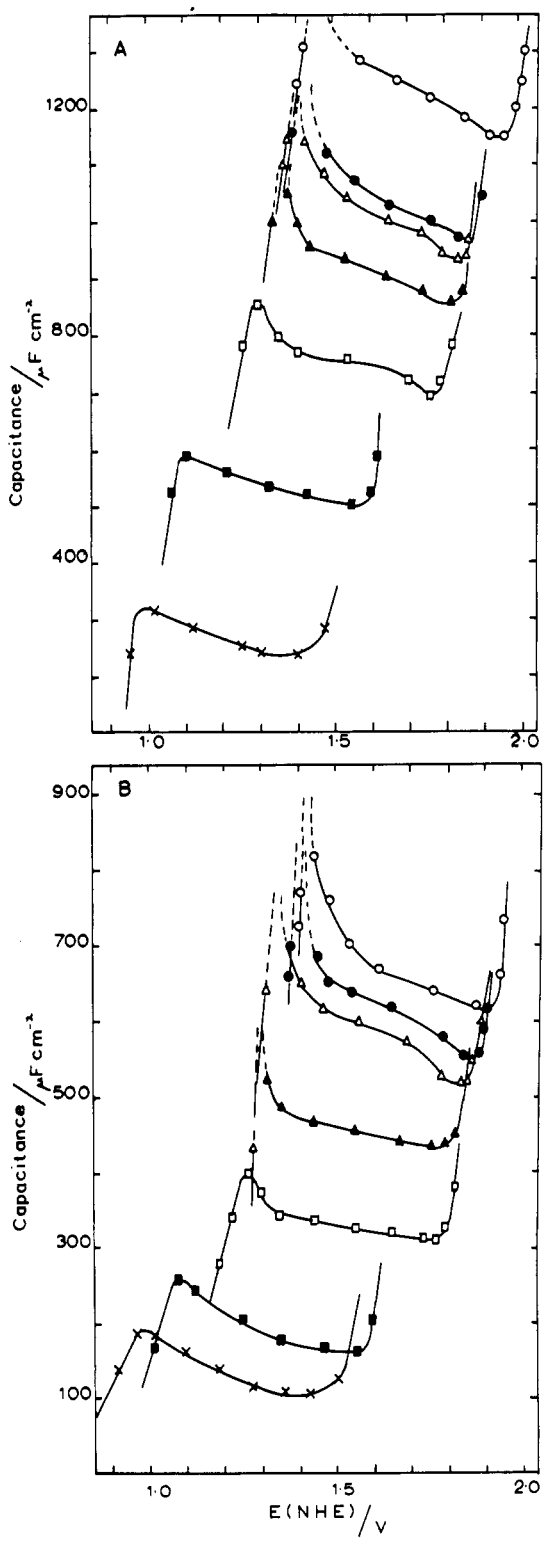

Figure 7. Differential capacitance *vs.* bias potential curves for electrodeposited α-lead dioxide (A) and β-lead dioxide (B) at 23°, 0.344 *M* aqueous K_2SO_4 over pH range 1–12: (×) pH 12.0; (■) pH 6.0; (□) pH 3.8; (▲) pH 3.4; (△) pH 3.0; (●) pH 2.5; (○) pH 1.8, frequency 120 Hz. From ref 139 by permission of the *Journal of Electroanalytical Chemistry*.

~40°. The magnitude of these enthalpies are of the order often observed for measurements of exchange reactions at electrodes; however, such measurements are of only limited significance because of the presence of unknown thermal junction potential. The change in slope of the Arrhenius plot at ~40° is particularly interesting because of a complementary behavior in the equilibrium measurements.

E. ELECTRODE REACTIONS IN SULFATE SOLUTIONS

Because of the great technological importance, a number of reviews of the reactions involved with this system, the positive plate of the lead acid battery, have been published. Those of Vinal[1] and Burbank, Simon, and Willihnganz[5] appear to be the most important of those presently available although other important summaries have from time to time appeared.[3,4] For the reader concerned mainly with the technology of the reaction, a combination of ref 2 and 5 appears to be adequately up to date, and the early work on the discharge mechanism has been adequately reviewed therein.

1. *Thermodynamics of the $PbO_2|PbSO_4$, H_2SO_4 Electrode*

The thermodynamic reversibility of the lead–acid battery, established beyond all doubt, requires that the positive plate is reversible for the reaction

$$PbO_2 + 4H^+ + SO_4^{2-} + 2e = PbSO_4 + 2H_2O \qquad (31)$$

for which at 25° for β-lead dioxide[121,122]

$$E_\beta = 1.6871 - 0.1182\text{pH} + 0.0295 \log a_{SO_4^{2-}} \qquad (32)$$

and for α-lead dioxide[121,122]

$$E_\alpha = 1.6971 - 0.1182\text{pH} + 0.0295 \log a_{SO_4^{2-}} \qquad (33)$$

and

$$(dE_\beta/dT)_p = -0.20 \text{ mV/°C, } 4.62\ M\ H_2SO_4 \qquad (34)$$

$$(dE_\alpha/dT)_p = -0.36 \text{ mV/°C, } 4.62\ M\ H_2SO_4 \qquad (35)$$

2. *Kinetics of the $PbO_2|PbSO_4$, H_2SO_4 Electrode*

The overall reaction expressed by eq 31 is well established; however, the reaction paths and charge transfer mechanisms are not yet completely settled, partly because two electrons take part in the overall reaction, whereas theory of electrode kinetics makes a single-electron transfer step much more likely, and partly because of the complications engendered by a layer of insoluble sulfate formed at the interphase. It should be mentioned in this connection that the existence of trivalent lead in a definite compound has never been observed and uncomplexed tetravalent lead ion is not detected in solution; however, Russian workers[158] have described the existence of a trivalent lead intermediate and indirect kinetic evidence for such a species has been presented elsewhere.[155–157]

Beck, Lind, and Wynne-Jones[121,122] have considered the reversible reaction from the thermodynamic viewpoint and conclude from their work that four reactions are thermodynamically impossible as components of the electrode exchange reaction; these are

$$H_2O \longrightarrow (OH) + H^+ + e \quad \text{(electrochemical)} \qquad (36)$$

(158) V. N, Varypaev and N. P. Fedot'ev, *Tr. Leningrad. Tekhnol. Inst. im Lensoveta*, **46**, 103 (1958).

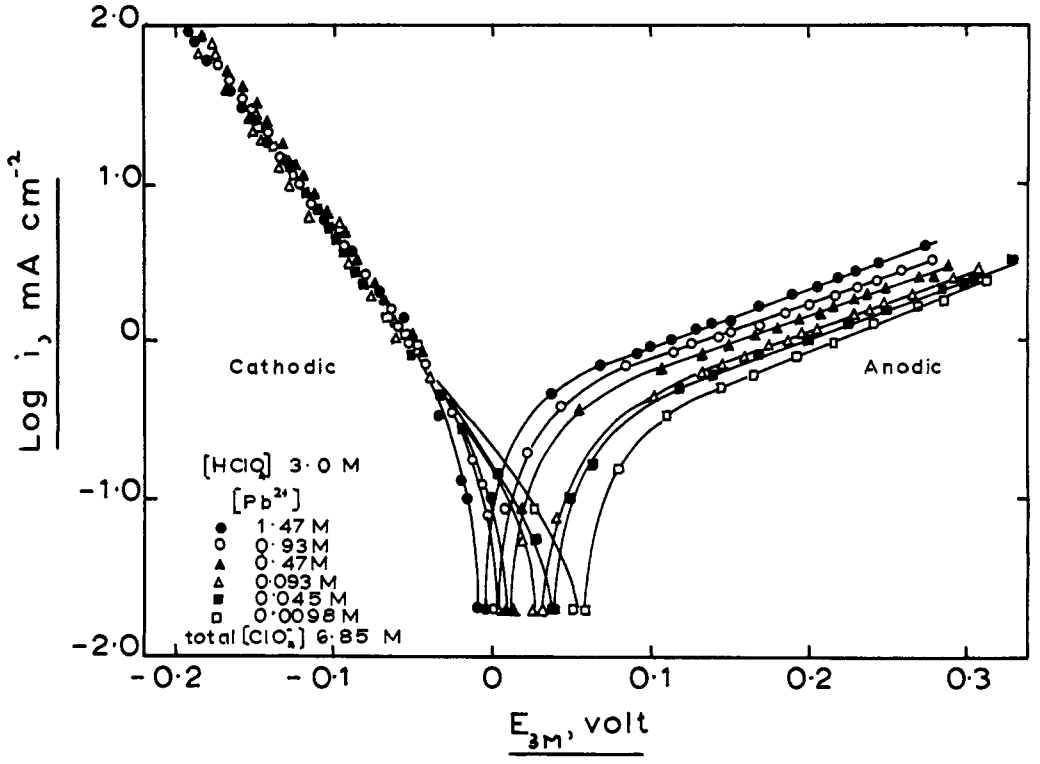

Figure 8. Anodic and cathodic current density–potential curves for electrodeposited β-lead dioxide at various Pb(II) concentrations in 3.0 *M* $HClO_4$ at 23°. From ref 156 by permission of the *Canadian Journal of Chemistry*.

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followed by

$$PbSO_4 + 2(OH) \longrightarrow PbO_2 + H_2SO_4 \quad \text{(nonelectrochemical)} \quad (37)$$

or

$$PbO_2 + 2e \longrightarrow PbO + O^{2-} \quad \text{(electrochemical)} \quad (38)$$

followed by

$$PbO + H_2SO_4 \longrightarrow PbSO_4 + H_2O \quad \text{(nonelectrochemical)} \quad (39)$$

since in order to obtain a thermodynamically reversible process the reaction mechanism cannot include any nonspontaneous nonelectrochemical step. It is well known that the mechanism of complete discharge of electrodeposited lead dioxide (in the energy conversion sense) in the presence of excess electrolyte involves passivation or blocking of the available surface of lead dioxide with a deposit of $PbSO_4$.[159] It has been emphasized by Burbank, *et al.*,[5] that attempts to analyze the kinetic reactions of charge and discharge on electrodes formed by anodic treatment of lead or of electrodeposited lead dioxide are complicated since the electrodes are a mixture of lead dioxide and $PbSO_4$. A kinetic study of battery plates is complicated because the reactions are diffusion controlled, and the varying porosity and composition give a surface difficult to maintain constant, notwithstanding other ions, *e.g.*, Sb(III), present at the electrode which may intrude on the lead dioxide|$PbSO_4$, H_2SO_4 reaction.

Fleischmann and Thirsk[160] studied the potentiostatic anodic oxidation of $PbSO_4$ to lead dioxide. At overpotentials of 0.1 V at 45° and 0.15 V at 15° no oxidation of the $PbSO_4$ layer occurred. At higher overpotentials, it was estimated that the voltage gradient across the $PbSO_4$ layer was of the order of 5×10^4 V/cm. At local centers of imperfection (active sites–growth sites) in the sulfate crystals, electrons were ejected, and these regions of high potential on the electrode surface acted as nucleation centers for lead dioxide. Two rate constants were determined: one for the rate of formation of nuclei of lead dioxide in the $PbSO_4$ layer, and, the other, a constant related to the rate of growth from a center, the square of the age of the nucleus, and the total possible number of nuclei. The "nucleation overvoltage" was a peak at the leading edge of the polarization curve. The two rate constants were qualitatively shown to be related to the consecutive processes of nucleation, spherical growth, and overlap of growing lead dioxide crystals in the $PbSO_4$ layer. Initiation of the growth began at the crystal–electrolyte interphase; however, the system was too complicated for a reaction mechanism to be abstracted from the electrometric data. For the growth of lead dioxide on $PbSO_4$, Fleischmann and Thirsk[160] reported that when sufficient nuclei had been produced, the rate of formation of additional nuclei was not significant. Conversely, Mark[151] showed that, after initial stages in the discharge had occurred, subsequent partial discharges of β-lead dioxide electrodes indicated that creation of new nuclei was not significant. Once the nucleation of $PbSO_4$ had occurred, Mark and Vosburgh[153] observed that overpotential for the discharge reaction was linear with current density and did not deviate from this relation until the electrode became passivated. This was interpreted as indicating direct reduction of lead dioxide to Pb(II), the rate-determining step being the transfer of two electrons. Mark investigated the reduction of α-lead dioxide and concluded that the mechanism differed from that of β-

(159) B. N. Kabanov, D. I. Leikis, and E. I. Krepakova, *Dokl. Akad. Nauk SSSR*, **98**, 989 (1954).
(160) M. Fleischmann and H. R. Thirsk, *Trans. Faraday Soc.*, **51**, 71 (1955).

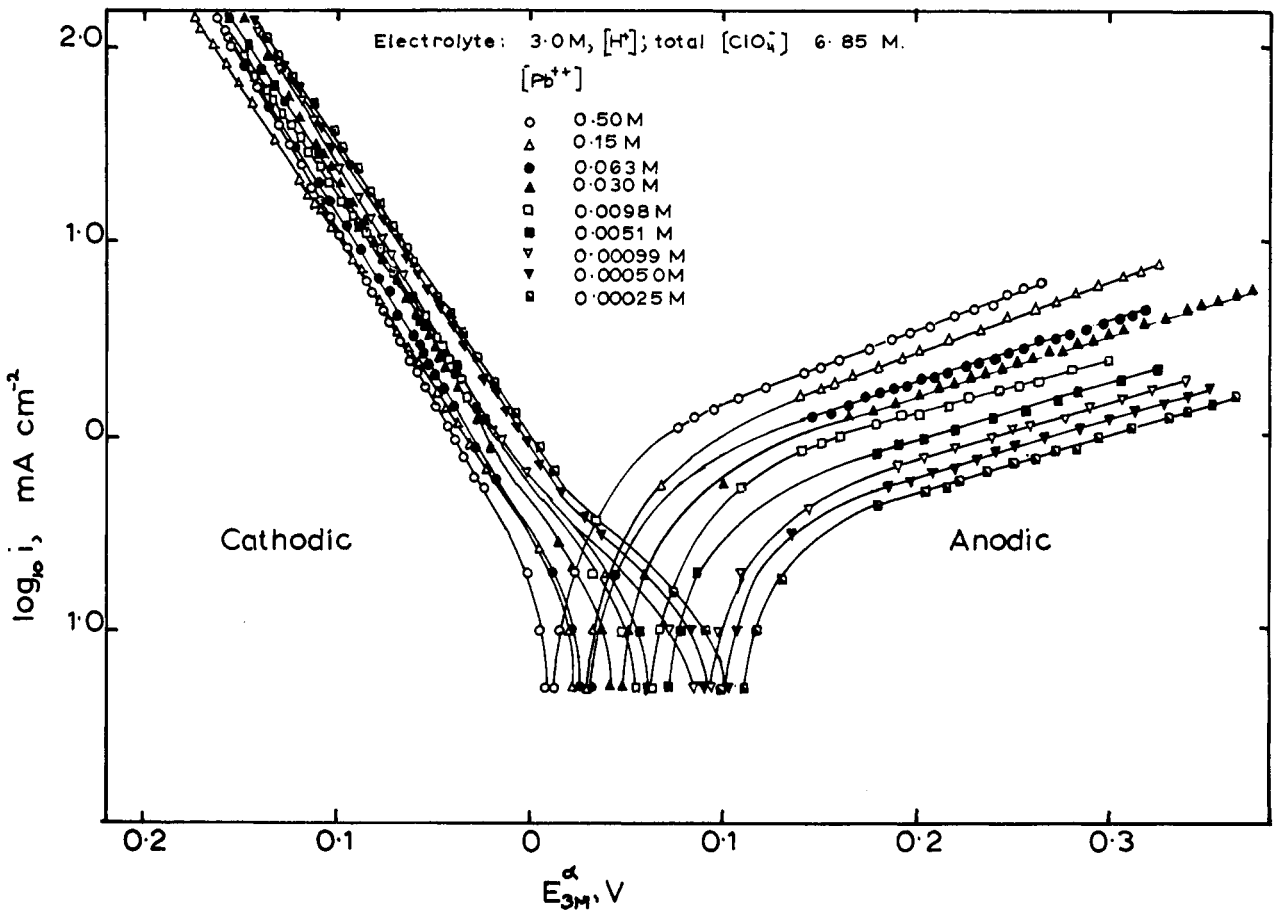

Figure 9. Cathodic and anodic current density–potential curves for electrodeposited α-lead dioxide at variable Pb(II) concentrations in 3.0 *M* H^+ at 23°; total [ClO_4^-] 6.85 *M*. From ref 157 by permission of the *Canadian Journal of Chemistry*.

lead dioxide. The $PbSO_4$ produced remained as a tightly adhering film on the surface of the undischarged α-lead dioxide in contrast to β-lead dioxide where it was distributed as crystalline nuclei. It was suggested that the α-lead dioxide reaction occurs on the surface whereas the corresponding product in the reduction of β-lead dioxide passes into solution and then deposits on existing $PbSO_4$ crystals. Ikari, *et al.*,[161] also noticed differences in the discharge behavior of α- and β-lead dioxide as did Voss and Freundlich[41] who reported that for α-lead dioxide the discharge capacity was lower than the β polymorph.

Wynne-Jones and coworkers[128,162,163] investigated the exchange between α- and β-lead dioxide and Pb(II) in solution using both radiometric and electrometric measurements. The exchange between Pb(II) in solution and Pb(IV) in the electrode at room temperature was attributed to the charging of the double layer and it was suggested, moreover, that at high temperatures the exchange is confined to disordered material in the vicinity of lattice imperfections. It was rigorously confirmed that the reaction occurring in the cell

$$(Pt)H_2|H_2SO_4\ (M),\ PbSO_4,\ PbO_2|(Pt)$$

was

$$PbO_2 + H_2SO_4 + H_2 \rightleftharpoons PbSO_4 + 2H_2O$$

for both α- and β-lead dioxide.

The application of impedance measurements to the lead dioxide–H_2SO_4 system has been made by Russian workers.[137,145] Experiments have largely been exploratory and have included measurements in the oxygen evolution region; however, no kinetic data were obtained. A later paper[164] describes an impedance study in which the exchange current was evaluated ($i_0 \sim 0.32$ mA cm^{-2}) which was in agreement with the value obtained by other workers[155–157] for perchlorate systems.

F. ELECTRODE REACTIONS IN PHOSPHATE SOLUTIONS

A discovery,[165] on the basis of a large number of *ad hoc* experiments, that addition of phosphoric acid to the conventional lead-acid cell electrolyte apparently improves the cycle life of the positive electrode is of some interest. The mechanism for the process cannot be regarded as settled. Feitknecht and Gaumann[101] suggested that intermediate plumbic compounds form during the charging process in the sulfuric acid accumu-

(161) S. Ikari, S. Yoshizawa, and S. Okada, *J. Electrochem. Soc. Jap.*, 27, E223 (1959).
(162) S. J. Bone, M. Fleischmann, and W. F. K. Wynne-Jones, *Trans. Faraday Soc.*, 55, 1783 (1959).
(163) M. Fleischmann and H. R. Thirsk, *Electrochim. Acta*, 1, 146 (1959).
(164) I. A. Aguf, *Elektrokhimiya*, 4, 1130 (1968).
(165) H. Bode and E. Voss, *Electrochim. Acta*, 6, 11 (1962).

lator which are not stable in the 40% (max) acid, but spontaneously decay or suffer hydrolysis

$$PbSO_4 + SO_4^{2-} + 2H_2O = \{[Pb(OH)_2(SO_4)_2]^{2-}\} + 2H^+ + 2e^- \quad (40)$$
$$\{[Pb(OH)_2(SO_4)_2]^{2-}\} = PbO_2 + H_2SO_4 + SO_4^{2-}$$

or

$$PbSO_4 + SO_4^{2-} = \{Pb(SO_4)_2\} + 2e^-$$
$$\{Pb(SO_4)_2\} + 2H_2O = PbO_2 + 2H_2SO_4 \quad (41)$$

However, Feitknecht and Gaumann[101] suggested that in the presence of additions of phosphoric acid, plumbous phosphate was formed at the electrode which was then oxidized to the corresponding plumbic phosphate, $H[Pb(OH)_2PO_4]$, which is relatively stable. It was shown by Bode and Voss that yellow plumbic phosphate (analytical composition $2PbO_2 \cdot P_2O_5 \cdot 2.5\text{–}3H_2O$) is formed in a maximum solution concentration at a molar ratio of $H_2SO_4:H_3PO_4 \sim 0.5$. At a molar ratio $H_2SO_4:H_3PO_4 < 0.5$ the yellow compound changes, by conversion, into a difficultly soluble white plumbite compound (analytical composition $PbO_2 \cdot P_2O_5 \cdot H_2O$). Under conditions where excess phosphoric acid is present, it is suggested that decomposition of the yellow compound with separation of pure α-lead dioxide takes place directly on the electrode surface owing to migration of H^+ ions into the solution. On the other hand, where excess sulfuric acid is present, hydrolysis processes bring about separation of the two lead dioxide modifications, but existence of the compounds $Pb(OH)_2SO_4$ or $Pb(OH)_2(SO_4)_2^{2-}$ is hypothetical in this case. It has been established by other workers that increased α-lead dioxide content in positive plates improves the cycle life.[5]

VII. Nucleation of Lead Dioxide

Frequently lead dioxide is deposited from solution onto an inert metal substrate. The process of the nucleation of such a layer has been considered in great detail by Fleischmann, Thirsk, and coworkers.[114,160,163] The process of electrodeposition of a new phase at an electrode involves the laying down of a number of nucleation centers followed by the growth of these centers until overlapping occurs when the growth centers coalesce to form a complete layer of the new phase. Fleischmann and Thirsk[163] have discussed the theoretical background to such depositions and the relationships connecting the deposition current density, and the times for conditions of constant potential have been fully formulated.

Two systems have been studied in depth: (i) the deposition from lead acetate solutions[114] and (ii) the formation of lead dioxide from lead sulfate.[160]

A. DEPOSITION OF LEAD DIOXIDE ONTO AN INERT BASIS FROM LEAD ACETATE SOLUTION

In these solutions it is known[44,45] that α-lead dioxide is predominantly deposited provided that the current density is not too high. Fleischmann and Liler[114] investigated the kinetics of deposition of α-lead dioxide from acetate solutions on a platinum basis. Measurements were made at constant values of the overpotential of the working electrode. The concentration dependence of the rate constants controlling the reaction were investigated. It was suggested that the formation of the lead dioxide in the nonsteady state was determined by the rate of formation of nuclei, an induction period before nucleus formation, and the rate of growth of formed centers. The potential and concentration dependence of these constants were studied. It was found that measurements of the initial stages of the nucleation process did not allow the rate equation to be extracted. By preforming nuclei the current rose more rapidly with time at low overpotential so that the growth process may be sufficiently separated in time from the nucleation process to obtain a limiting value of initial current above which the rate (current) at low overpotential becomes independent of the time of the preformation step. At low overpotential it was shown that the current varied as the square of the time

$$i = N_0 B_3 t^2 \quad (42)$$

where N_0 is the original maximum number of nuclei on unit surface and B_3 a potential dependent growth constant and three-dimensional growth is indicated. Fleischmann and Liler[114] suggested that before nucleation occurred an induction period is necessary and the current–time relationship

$$i = \frac{AB_3N}{3}(t - t_0) \quad (43)$$

where t_0 is the induction period, is observed. From the variation of current density with concentration at fixed potential, the orders of reaction with respect to the plumbous and hydroxyl ions were obtained and found to be nonintegral. It was consequently suggested that the slow stage of the reaction was

$$Pb^{2+} + OH_{ads} + OH^- - e \longrightarrow Pb(OH)_2^{2+} \rightleftharpoons PbO_2 + 2H^+ \quad (44)$$

and that the deviations of the reaction orders from whole numbers were due to adsorption on the electrode surface. Fleischmann and Liler[114] noted that the nucleation constants increased and the variation of the slopes of nucleation rates with overpotential decreased with decreasing reversible β-lead dioxide potential. These facts were interpreted as indicating an increase in the surface free energy of lead dioxide with increasing potential.

B. NUCLEATION OF LEAD DIOXIDE ONTO $PbSO_4$

The formation and growth of lead dioxide deposits on $PbSO_4$ bears some similarity to the deposition of lead dioxide from acetate solution. Thus it is necessary to form lead dioxide nuclei which act as active centers for the spreading of lead dioxide through the bulk of the material. Fleischmann, Thirsk, and coworkers have considered the conversion of lead sulfate to lead dioxide in some detail.[160,163] The current–time data were found to obey a cubic law of the form

$$i = ABt^3/3 \quad (45)$$

where B is a potential dependent constant, A is the nucleation constant, and t is time. The rate of the oxidation was found to reach a maximum and then exponentially decay. It was assumed that the growth of a β-lead dioxide center was confined to discreet single lead sulfate crystals and that the decay was due to the completion of the reaction. The relationship connecting the number of nuclei and time (the nucleation) was shown to be

$$N = N_0(1 - \exp(-At)) \quad (46)$$

where N is the number of nuclei on unit surface and N_0 the maximum number of nuclei on unit surface.

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It was possible to derive two rate equations: when $t < t_{max}$

$$i = B_3N_0\left(t - \frac{2t}{A^2} + \frac{2}{A^2} - \frac{2}{A^2}\exp(-At)\right) \quad (47)$$

and when $t > t_{max}$

$$i = B_3N_0 \exp[-A(t - t_{max})] \times \left(t^2_{max} - \frac{2t_{max}}{A} + \frac{2}{A^2} - \frac{2}{A^2}\exp(-At_{max})\right) \quad (48)$$

Using similar reasoning to that used for the deposition of α-lead dioxide from acetate solutions, it was found that the surface energy of β-lead dioxide increased with potential. For both the oxidation of $PbSO_4$ to β-lead dioxide and oxidation of plumbous salts to α-lead dioxide, the variation of nucleation rate with overpotential obeyed the relationship

$$A = ki_0 \exp(-\kappa\sigma^3/\eta^2) \quad (49)$$

where k is a frequency factor, i_0 the exchange current, κ a constant determined by the shape of the nucleus, and σ the surface energy.

C. OXIDATION OF LEAD TO LEAD DIOXIDE

Because of its prominent position in present day commerce, the lead–acid Plante cell has been studied in considerable detail. The reaction of paramount importance to this and the lead–acid cell generally is the formation of lead dioxide on a lead substrate, and it was considered sufficiently important to present day technology to warrent a fairly detailed review of this aspect of the lead dioxide electrode.

A large number of workers have studied the anodic oxidation of lead electrodes in H_2SO_4.[69,84,161,166–213] Constant current charging curves[69,84,161,166–181] on closing the electrical circuit show an immediate rise in potential to a potential plateau. Haring and Thomas[203] showed that the initial potential was that of the reversible Pb|$PbSO_4$ electrode. The potential then rises to a potential peak above the $PbSO_4$|lead dioxide potential. Few workers have observed an intermediate potential arrest between the Pb|$PbSO_4$ redox potential and that of the $PbSO_4$|lead dioxide electrode; however, Ekler[170] inferred a potential inflection occurring at the Pb|PbO or Pb|$Pb(OH)_2$ potential, and Lander[182] suggested that at potentials below the reversible lead dioxide|$PbSO_4$|H_2SO_4 electrode, the lead surface was oxidized with the formation of a layer of PbO on the lead and a layer of $PbSO_4$ next to the electrolyte. Between the Pb|$PbSO_4$ potential and $PbSO_4$|lead dioxide potential the sharp potential peak in the charging curve has been associated with the difficulty of nucleation of lead dioxide on the $PbSO_4$ layer.[160] Ikari and Yoshizawa[171] suggested that the peak was due to the formation of poorly conducting oxides lower than lead dioxide, and Feitknecht and Gaumann[101] associated the potential peak with the conversion of $PbSO_4$ to lead dioxide by reaction with OH radicals. At the $PbSO_4$|lead dioxide potential a plateau is observed in the charging curves in which O_2 is evolved on the lead dioxide surface and lead dioxide is continuously formed by anodic oxidation of the metallic Pb.[69,121,161,168,170,180] Lander[182] showed that the anodic oxidation of lead was a maximum as the potential approached +1.25 V and a minimum at 1.45–1.75 V (formation of a protective layer of lead dioxide). Further work by Lander[183] showed that lead dioxide and Pb underwent a solid phase reaction

$$PbO_2 + Pb = 2PbO \quad (50)$$

and suggested that cracks develop which allow reaction between the lead and the electrolyte facilitating the oxidation process. At potentials below that of the $PbSO_4$|lead dioxide potential Lander[116] suggested that lead dioxide may be formed but is unstable and is converted to PbO and $PbSO_4$. At potentials close to the $PbSO_4$|lead dioxide potential $PbSO_4$ is

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formed, and at the $PbSO_4$|lead dioxide potential lead dioxide forms and oxidation becomes minimal.

In alkaline solutions the charging curves show an initial potential plateau due to the formation of PbO.[172] Burbank[210] suggested that the PbO had a distorted tetragonal lattice and was more reactive than litharge or massicot. At higher potentials, Pb_3O_4 and $Pb_{12}O_{19}$ were formed so that a layer composed of a mixture of the three oxides was obtained before a potential peak is reached. After the peak lead dioxide was nucleated, PbO was converted to α-lead dioxide. The lead dioxide is present at a loosely held film which can be flaked off to expose an orange layer of the lower oxides underneath. It has been suggested that the oxidation process on lead in alkaline solutions occurs by a two-electron exchange mechanism.[182,183,204,210]

$$Pb + 2OH^- = PbO + H_2O + 2e \quad (51)$$

Part of the PbO is then oxidized to α-lead dioxide

$$H_2O = (O)_{ads} + 2H^+ + 2e \quad (52)$$

$$PbO + (O)_{ads} = PbO_2 \quad (53)$$

At potentials above the O_3–H_2O potential, lead oxidizes directly to lead dioxide by a tetravalent mechanism.

In H_2SO_4, both α- and β-lead dioxide are products of the oxidation of lead;[69,84,125,199] however, it has been shown that the α-lead dioxide is adjacent to the metal[190,191,199] and that oxygen is able to penetrate the β-lead dioxide layer to react with the underlying Pb.[211] Experiments[212] with labeled (^{35}S) SO_4^{2-} ions showed that films of $PbSO_4$ were ionic conductors and that Pb(II) ions may move across the interphase by a process of solid phase diffusion. Other workers[167,184] have suggested a complicated double salt constitution for the electrode layers. Evidence is largely from X-ray diffraction carried out on electrodes withdrawn from the electrolytic cell so that it is often difficult to judge whether results correspond to the electrode situation or to an isolated dried electrode. Since $PbSO_4$ forms a protective layer permeable to H^+ ions and H_2O molecules but not to SO_4^{2-} ions,[180,183,189] an alkaline condition may be maintained next to the Pb interface which explains the detection[182,183] of PbO on lead anodes in acid solutions. Ruetschi[180] also indicated that alkaline conditions can be set up behind the $PbSO_4$ films so that PbO or basic lead sulfates may be formed at the Pb interface. As soon as the formation of α-lead dioxide is complete, O_2 evolution occurs and it is now agreed that the form of lead dioxide produced by the oxidation of $PbSO_4$ is the β variety; however, α-lead dioxide is formed next to the lead interface in a region of high pH.

It can be concluded from the very large number of investigations that this complex reaction proceeds by the transport of charge and mass through a multiplex polyphase boundary and that the penetration of atomic oxygen from the solution side toward the metal is a major process. The study of the morphology of developing layers by potential arrest techniques is consequently likely to be greatly complicated since the potentials which are obtained depend on the role and concentration of the atomic oxygen at the interphase.

In the formation of lead dioxide on Pb by anodization in H_2SO_4, Burbank[168] has shown that the (100) plane of β-lead dioxide lattice was oriented parallel to the (100) plane of the base. It follows that there exists a 21% mismatch in unit cell dimensions which would cause fracture of growing layers in order to relieve the stress produced. Cahan and Ruetschi[200] studied the polarization of a Pb anode by superimposing an ac square wave current on the steady direct current and determined the impedance along with the potential as a function of time. When the cathodic circuit was closed, the potential dropped from the oxygen overpotential to the lead dioxide–$PbSO_4$ potential, and the double layer capacity was very high (500–1000 $\mu F/cm^2$). After the lead dioxide step, a short arrest appeared between −0.1 and −0.2 V, and the capacity fell to a very low value. This step in the discharge curve may be associated with the presence of the poorly conducting PbO, $Pb(OH)_2$, or basic lead sulfates; subsequently, a long $PbSO_4$ plateau is reached with a capacity value of about 75 $\mu F/cm^2$ followed by H_2 evolution. In alkaline solutions, the discharge curve exhibits steps associated with the PbO|$PbSO_4$ and the Pb|PbO potentials before H_2 evolution is reached. A small overshoot is detected just ahead of the PbO plateau. Jones and coworkers[175] suggest that a plateau following the $PbSO_4$ step is associated with a lead hydride.

D. LINEAR SWEEP VOLTAMMETRY

Linear sweep volammetry (LSV) techniques would be expected to yield data complementary to the measurements discussed in the previous sections. However, there have been few reported studies on lead dioxide. Chartier and Poisson[214] studied the cathodic reduction of β- and α-lead dioxide in alkali and found that the mechanism of the reduction differed for the two polymorphs. For β-lead dioxide it was suggested that the electrode reaction mechanism consisted of two processes: (a) a solution reaction

$$\beta\text{-}PbO_2 + H_2O + 2e = HPbO_2^- + OH^-$$

and (b) a solid-phase reaction

$$\beta\text{-}PbO_2 + H_2O + 2e = PbO + 2OH^-$$

For α-lead dioxide they suggest that the reduction process occurs exclusively in the solid phase but were unable to give an exact mechanism.

Recently Carr and Hampson[142] made LSV studies on α- and β-lead dioxide in alkali using faster sweep speeds than Chartier[214] (~12 mV sec^{-1}). Figures 10A and 10B show typical cathodic potential sweep scans for α- and β-lead dioxide, respectively. For α-lead dioxide it was shown that, for the peak corresponding to the lead dioxide reduction a linear relationship between I_m and $\sqrt{v}$ was observed passing through the origin indicating that the current-limiting relationship is that of diffusion of OH^- ions in solution. From the dependence of I_m on [OH^-], they concluded that adsorption of electrode products intrudes in the electrode reaction. The suggested sequence of reactions involved the scheme

$$\alpha\text{-}PbO_2 + H_2O + 2e = PbO_{ads} + 2OH^- \quad (54)$$

$$PbO_{ads} = PbO_{aq} \quad (55)$$

$$PbO_{aq} + OH^- + H_2O = Pb(OH)_3^- \quad (56)$$

Calculation of the diffusion coefficient from their results yields a value of $\sim 10^{-7}$ cm^2 sec^{-1} which is too small to be the true diffusion coefficient of the OH^- ion in aqueous solution. These data can be interpreted by either of two explanations: diffusion of OH^- ions must occur through a layer of anodic products and the diffusion coefficient involved was that of the diffusing ion in the product phase; or, alternatively, the true surface area of the electrode available for diffusion was very

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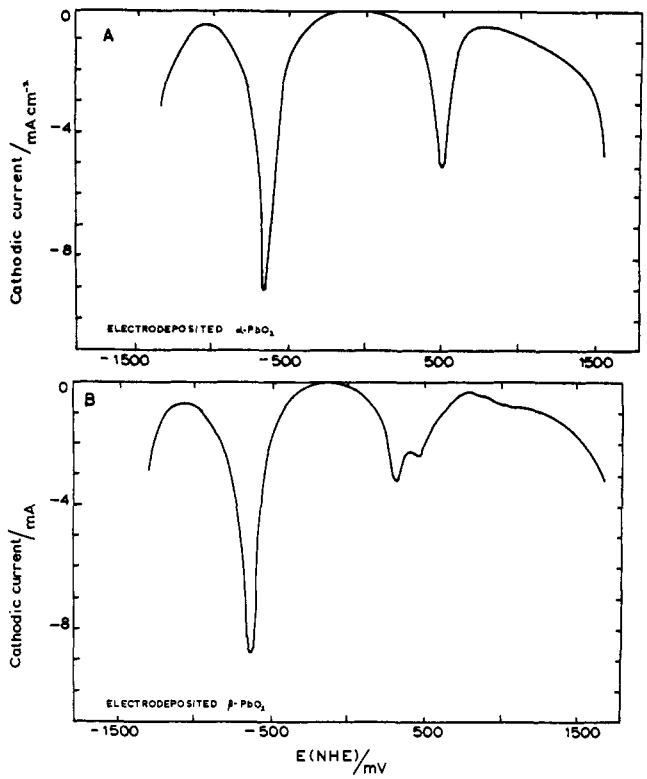

Figure 10. Typical fast cathodic potential sweep on electrodeposited α-lead dioxide (A) and β-lead dioxide (B) in aqueous NaOH solution (4.7 *M*), 23°, sweep rate 58.3 mV sec^{-1}. Electrode area 4.9 × 10^{-2} cm^2. From ref 142 by permission oft he *Journal of the Electrochemical Society.*

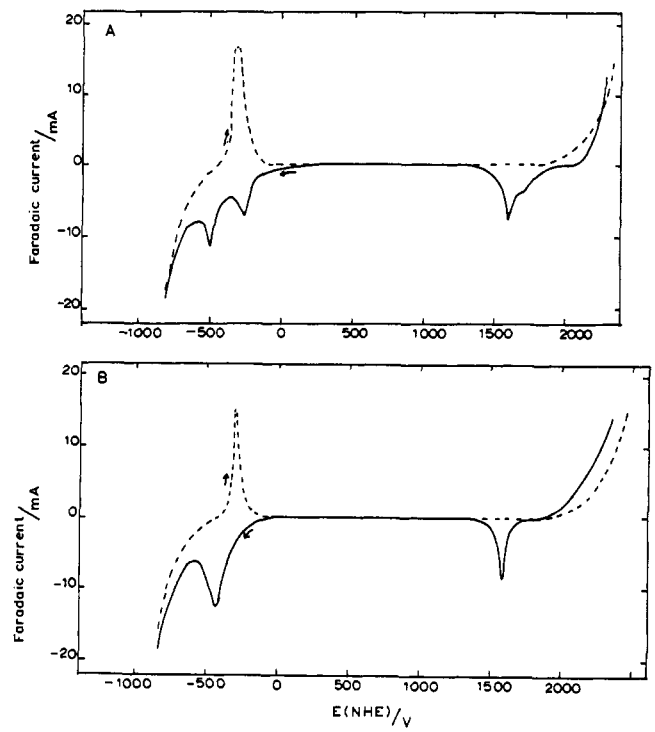

Figure 11. Typical current-potential curve for a cathodic (—) and anodic (----) potential sweep on electrodeposited α-lead dioxide in 4.41 *M* aqueous H_2SO_4 solution (A) and β-lead dioxide in 5.56 *M* H_2SO_4 solution (B) at 23°. Electrode area 4.49 × 10^{-2} cm_2; sweep rate 58.3 mV sec^{-1}. From ref 215 by permission of the *Journal of Electroanalytical Chemistry.*

much less than the apparent area due to the presence of a solid phase of PbO. It was found difficult to decide whether the explanation of an adsorbed layer through which the OH^- ion must diffuse was better supported by previous experimental work than was the postulation of an incomplete oxide film. For β-lead dioxide at the lead dioxide|PbO potential, two peaks were observed indicating the presence of α-lead dioxide in the deposit. Continuous cathodic cycling showed a decrease in peak f but an increase in peak g, indicating a possible modification of the β-lead dioxide on the electrode surface to α-lead dioxide.

Carr, Hampson, and Taylor also reported LSV measurements in H_2SO_4[215] solutions. For β-lead dioxide Figure 11B shows a typical fast cathodic sweep trace. At the lowest of the sweep speeds applied, a linear relationship between I_m and $\sqrt{v}$ was observed for the lead dioxide → $PbSO_4$ reaction passing through the origin. I_m was directly proportional to the concentration of H_2SO_4 throughout the whole of the experimental concentration range, indicating that the faradaic current flow was controlled by a diffusion process in solution. The diffusion coefficient determined from these results ~10^{-4} cm^2 sec^{-1} was considerably higher than that reported for the SO_4^{2-} ion, but it was suggested that this was due to the electrode being "rough," as would be expected for such an electrode. At higher sweep speeds an abrupt change in the slope of the I_m *vs.* $\sqrt{v}$ relationship was observed which occurred at progressively lower sweep speeds for increasing H_2SO_4 concentrations and gave significant intercepts on the current axis. It was suggested that there were two separate mechanisms of current limitation other than charge-transfer limitation, namely (i) limitation due to shortage of SO_4^{2-} ions at the electrode and (ii) limitation due to the passage of charge through the insoluble layer of $PbSO_4$. At lower sweeping speeds and low H_2SO_4 concentrations the current limiting process was the diffusion of the SO_4^{2-} ion in solution to the electrode interphase and at higher sweeping speeds and/or higher concentrations of H_2SO_4 the current limitation was due to the diffusion of ions in a film of $PbSO_4$ at the electrode surface. For α-lead dioxide Figure 11A shows a typical fast cathodic potential scan. Repetitive cycling between the limited potential range +2200 to +1400 mV, with negligible rest time between sweeps, showed a progressive increase of the current shoulder and decrease of the main peak for the lead dioxide → $PbSO_4$ reaction. In contrast to β-lead dioxide, results of plots of I_m (peak e) *vs.* $\sqrt{v}$ did not give linear relationships and indicated that a process other than diffusion was also involved at the electrode at this potential. For example, in acid electrolytes α-lead dioxide undergoes structural modifications at its surface to give more stable β-polymorph in low pH electrolytes.

$$\alpha\text{-}PbO_2 \overset{H^+}{\rightleftharpoons} Pb(IV) \rightleftharpoons \beta\text{-}PbO_2 \qquad (57)$$

Repetitive sweeps in acid solutions tended to increase the proportion of β-lead dioxide at the α-lead dioxide electrode surface until the β-polymorph was the dominant form involved in the reduction process. A tentative explanation of the appearance of two peaks at the $PbSO_4$ → Pb potential for α-lead

(215) J. P. Carr, N. A. Hampson, and R. Taylor, *J. Electroanal. Chem.*, 33, 109 (1971).

dioxide but not β-lead dioxide was the reduction of some lead compound underneath the $PbSO_4$ layer.

Panesar[216] also studied the cathodic reduction of α- and β-lead dioxide by LSV but used very slow sweep speeds. Cathodic sweeps were made from +1600 mV as shown in Figure 12. The peak at ~−800 mV was observed only in the case of α-lead dioxide; also, for the anodic sweep no current maximum occurred which could indicate the oxidation of $PbSO_4$ → lead dioxide. However, by cycling between +1700 and 800 mV, both the reduction and oxidation reactions were observed. Cycling also caused the oxidation–reduction peaks for α-lead dioxide to move to negative potentials, but those of β-lead dioxide remained constant indicating the conversion of α-lead dioxide to β-lead dioxide.

VIII. Oxygen Evolution on Lead Dioxide Electrodes

Only in H_2SO_4 solution has the oxygen evolution reaction (oer) at lead dioxide electrodes been investigated thoroughly.[10,39,40,84,180,217-236] It is well known that oxygen is evolved from a lead anode only when a layer of lead dioxide has been laid down[204] and that the overpotentials are relatively high,[2] being ~0.8 V at ~1 μA cm^{-2}. Quantitative data in H_2SO_4 electrolytes have been obtained by Ruetschi and coworkers.[39,40,84,218-221] It was found necessary to preanodize the electrodes at potentials more positive than that corresponding to the oxygen evolution potentials in order to obtain a time-stable electrode. The reaction was shown to be slow; exchange currents for the α-polymorph were reported to be 1.77×10^{-16} A cm^{-2}, and for β-lead dioxide 6.2×10^{-10} A cm^{-2} in 4.4 *M* H_2SO_4.[39,40] Ruetschi and coworkers used electrodeposited lead dioxide on glass-sealed Pt rods for these measurements, and it is clear from their results that either the β-polymorph is much more catalytically active for the oer than the α form or that the morphology of the

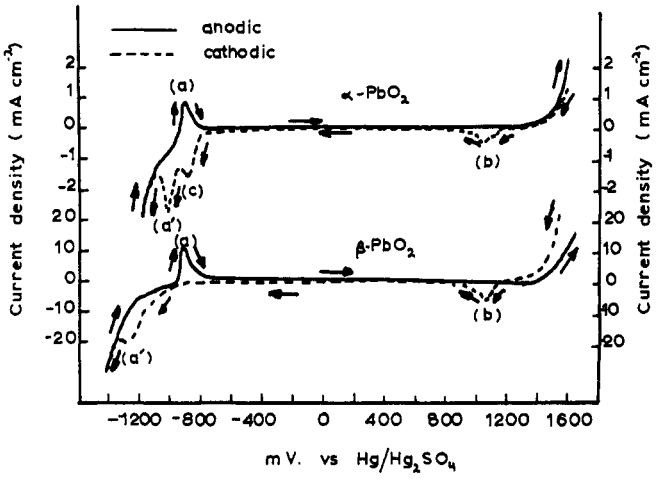

Figure 12. Cyclic voltammetric curves for α- and β-PbO_2 electrodes in 5 *M* H_2SO_4 at 30 mV/min: (—) anodic, (----) cathodic. From ref 216 by permission of Oriel Press.

polymorphs is completely different. On the basis of capacitance results, it seems to be clear that surface area factors cannot explain these differences. It has been reported[192] that using specially prepared α- and β-lead dioxide electrodes of very low surface area identical kinetics are obtained for the oer; however, data are lacking as to exactly what was done in order to obtain this agreement. It is interesting to note that in H_2SO_4 electrolytes the experimentally determined equilibrium potential for the lead dioxide electrode corresponds to the lead dioxide|$PbSO_4$, H_2SO_4 potential rather than the oxygen potential. This can be traced to the presence of a layer of $PbSO_4$ on the surface of the electrode which is further evidence that the SO_4^{2-} ion, in some form or another, is adsorbed on lead dioxide. The value of the Tafel slopes for the oer on lead dioxide has been reported in the region of 0.1–0.15 V/decade. For β-lead dioxide it is generally found that the Tafel slope is higher than that on α-lead dioxide. Hoare[4] considers it significant that for β-lead dioxide a slope of ~0.12 V/decade is typical of the oer on metals, whereas for α-lead dioxide a slope of ~0.05 V/decade observed by Ruetschi and coworkers corresponds to the oer on metals in alkaline solution. It cannot be completely ruled out that the morphology of the electrode surface in the sense of Frumkin[237] and de Levie[6] may cause this difference which mainly arises from the effective nonuniform current distribution over the electrode surface. The oer on lead dioxide in common with the oer on most metals has a negative temperature coefficient of overpotential. The small value of the exchange current and the magnitudes of the Tafel slopes show that the oer is controlled by the charge-transfer process. Ruetschi and Cahan[39,40] suggest that the magnitude of the Tafel slopes indicates a two-electron change involved in the rate-determining step for the oer on α-lead dioxide, whereas for the β-lead dioxide the rate-determining reaction involves only a one-electron transfer.[220] Other various reaction mechanisms have been proposed. Krasil'shchikov[230] suggests that the evolution of O_2 involves the discharge of OH^- ions or H_2O molecules to form absorbed O^{2-} ions. These O^{2-} ions convert the lead dioxide to a higher oxide which decomposes, as suggested by Glasstone,[224] to yield O_2 and lead di-

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oxide. However, lead dioxide cannot be oxidized to a higher state of oxidation,[218] and this mechanism is not favored for the evolution of O_2 on Pb anodes. It is interesting in this connection to note that Burbank[210] observed O_2 evolution on Pb anodes only at potentials more positive than the O_3/H_2O potential; at lower potentials lead corroded *via* lead monoxide in preference to O_2 evolution. Above the O_3/H_2O potential direct formation of lead dioxide takes place as a consequence of the corrosion of Pb without passing through the lead monoxide stage and O_2 is evolved. It is now established beyond doubt that an oxide of lead higher than lead dioxide does not exist so that lead dioxide acts as an inert electrode, and, by analogy to the mechanism proposed for the oer on noble metals, mechanisms have been proposed which fit most of the observed facts; *viz.*, H_2O molecules or OH^- ions react to give OH radicals at the electrode to form oxygen atoms

$$H_2O = OH_{ads} + H^+ + e \quad (58)$$

and

$$2OH_{ads} = O_{ads} + H_2O \quad (59)$$

followed by

$$2O_{ads} = O_{2,gas} \quad (60)$$

It is reasonable to suggest from the Tafel curves that the electron-transfer step is rate determining.[175] It has been observed experimentally, presumably from the combination of oxygen atoms in eq 60, that oxygen atoms are able to diffuse into the lead dioxide layer.[221,238] Russian workers[137] have applied the impedance technique to a study of the oer at lead dioxide electrodes. It is concluded that although the general kinetic behavior is similar to an inert metal, the highly developed surface covered with a layer of intermediate products to some extent complicates the picture. It was confirmed that the product of the charge-transfer reaction was OH_{ads}, which may then react to form oxygen.

In alkaline solution less experimental data are available than in the corresponding H_2SO_4 solution; however, Jones *et al.*,[175] have obtained overpotential–current density curves on lead anodes similar to those obtained in acid solutions although some deviations from Tafel behavior were observed at low current densities. Over most of the experimental region a slope of ~0.12 V/decade was obtained. The deviations could be ascribed to self-discharge between lead dioxide and the underlying Pb.

A. USE OF ELECTRODEPOSITED LEAD DIOXIDE FOR PREPARATIVE ELECTRODES

Lead dioxide prepared electrolytically has been used from time to time to make anodes suitable in preparative chemistry. Thus iodine has been anodized to periodic acid using both supported[239–242] and unsupported[243–255] (massive) lead dioxide electrodes with high current efficiencies; sodium chlorate has been anodically oxidized to sodium perchlorate in high yield[255] using lead dioxide electrodes of a number of different constructions; iodoform has been prepared[256,257] using the reaction of acetone or ethanol at an anode in the presence of the iodide ion. In all of the investigations reported so far lead dioxide behaves as an inert electrode in much the same way as Pt rather than showing any specific electrode catalytic activity. It is clear that lead dioxide is able to withstand prolonged high positive potentials more effectively than graphite (which undergoes degradation) and at the same time is cheaper than platinum and may be readily electrodeposited.

B. SELF-DISCHARGE OF LEAD DIOXIDE ELECTRODES

One shortcoming of the preparation of lead dioxide electrodes on a Pb basis is that reaction between the lead dioxide and the underlying Pb lattice is able to proceed in the solid phase. Because of the high electronic conductivity of lead dioxide, electron exchange facilitates the formation of Pb(II) ions able to react with O^{2-} ions to form a nonconducting PbO layer.

IX. Concluding Remarks

Lead dioxide is polymorphic and two forms (α and β) are well defined. Each variety may be prepared substantially free of the other provided that conditions are carefully controlled. The most convenient methods of preparation are based on the anodic electrodeposition from Pb(II) solutions. Lead dioxides never conform exactly to "PbO_2"; a small oxygen deficiency is always observed.

Well-established thermodynamic data exist concerning α- and β-lead dioxides; β-lead dioxide has a greater free energy of formation than α-lead dioxide. Lead dioxides have a high electrical conductivity which may well be connected with the oxygen deficiencies in their formulas. The high conductivity makes lead dioxide electrodes relatively accessible to study by electrometric methods.

The adsorption of various species at lead dioxide appears to be important in the kinetic behavior, particularly in the industrially important systems, involving sulfate and phosphate ions. The adsorption of hydrogen ion at the electrode in these two systems may well be connected with the polyhydric nature of sulfuric and phosphoric acids. In other electrolyte systems adsorption of solution species may also be pro-

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nounced, and aqueous potassium nitrate appears to be the only electrolyte in which adsorption is absent. Further work concerning adsorption phenomena at lead dioxide electrodes would be of great interest.

Exchange reactions at lead dioxide electrodes indicate relatively low values of exchange current density. Kinetic studies support the view that a neutral entity crosses the double layer in preference to a highly charged ion. Further work on these aspects would be of interest particularly since the system provides a cathodic analogy to metal dissolution.

The nucleation and growth of lead dioxide both in the case of the conversion of an insoluble layer of a Pb(II) salt and the anodic electrodeposition from homogeneous Pb(II) solutions warrant further study. The pioneering studies of the Newcastle group could well be extended in the light of recent advances in both theory and technique presently available. The exact nature of a "growth site" in the case of the lead dioxide electrode is of fundamental interest.

The kinetics of the oer on lead are as yet unsettled, and some explanation of the variability observed by various workers is required. Industrially the rate of corrosion of lead (and more particularly lead–antimony alloys), in the oxygen evolution region, in electrode systems of the type Pb|lead dioxide|H_2SO_4, O_2 is of paramount importance.

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